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INFLUENCE OF SECONDARY SCATTERING ON DEPOLARISATION MEASUREMENTS

By R. S. Krishnan
(Trinity College, Cambridge)

Received March 25, 1939
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

As is well known, one of the most useful methods for the determination of the size, shape and structure of particles in colloidal suspensions is that based on the study of the Tyndall scattering in the solutions. Such a study includes the measurement of the intensity and state of polarisation of the light scattered by the colloidal solution in a direction perpendicular to the incident beam. Using incident unpolarised light as also light polarised with vibrations respectively vertical and horizontal three different measures of the state of polarisation or the so-called depolarisation of the transversely scattered light are obtained, namely, ρ_u, ρ_v and ρ_h. These three quantities are related to the size, shape and structure of the particles contained on the solution and hence from a knowledge of their magnitudes it is possible to estimate the size, shape and structure of the scattering particles. This is true so long as the individual particles scatter quite independently of one another and the *macroscopic* depolarisation factor, *i.e.*, the depolarisation of the light scattered by the solution in bulk is equal to the *microscopic* depolarisation factor characteristic of the light scattered by any individual particle under the action of the incident light. But in most cases the conditions stated above are not satisfied as is evident from the fact that the values of ρ_u, ρ_v and ρ_h are influenced to a marked extent by the concentration of the colloidal solution. It is found that the values of ρ_u, ρ_v and ρ_h decrease progressively with increasing dilution and reach limiting values equal to the corresponding values of the individual particles. This dependence on concentration arises from two causes :—(1) the existence of a molecular field surrounding the particles and (2) the presence of secondary scattering. Gans (1920) considered the effect of molecular field on any particle inside the scattering medium arising from the dipoles induced in the neighbouring particles under the action of the incident electric vector and derived an expression for the macroscopic depolarisation factor in terms of the concentration, for colloidal solutions containing small ellipsoidal particles. Gans' formula indicates

that this effect due to the molecular field could be neglected if the concentration of the colloidal solution is small and the refractive index of the dispersed phase is not far different from that of the dispersing medium.

The second and more important cause for the dependence of the macroscopic depolarisation on concentration is the existence of what is known as secondary scattering. Rousset (1936) emphasised the importance of considering the effect of secondary scattering in depolarisation measurements. Each individual colloidal particle under the influence of the intense primary scattering from all the particles which are illuminated by the incident beam becomes a luminous source and scatters radiation in all directions. This process is called secondary scattering. In the case of colloidal solutions of low scattering power the secondary scattering is quite negligible, whereas in the case of emulsions and protein solutions where the scattering is very intense the secondary scattering becomes comparable in intensity. The presence of secondary scattering in such solutions can be easily demonstrated by passing a narrow beam of light through the solution. If one observes the scattered track in the transverse direction one finds the whole volume of the solution luminescent. The scattered track is superposed on an intense background the intensity of which is maximum along the track and fades off as one moves away from it on either side. The depolarisation of this background illumination which is due to secondary scattering is different at different points in the scattering medium (Krishnan, 1937 and Lotmar, 1938), and is always greater than that of the scattered track (primary scattering). In such cases, therefore, the observed depolarisation is the resultant effect of the depolarisations of the primary scattering and of the secondary scattering in the region of observation. The secondary scattering in a small element of volume is proportional to the number of particles contained in it and also to the total intensity of primary scattering which itself is proportional to the concentration. The intensity of secondary scattering is therefore proportional to the square of the concentration. This explains why the dependence of depolarisation on concentration is very marked in emulsions which are so dilute that the molecular field does not come into play.

In the case of simple dipole oscillators the intensity of secondary scattering and the depolarisation arising thereform, can be calculated by applying Rousset's theory (Rousset, 1936). For the most general case of large ellipsoidal particles the theory of secondary scattering is rather complicated and has not been fully worked out. It was, however, thought desirable to investigate this problem experimentally and to suggest ways and means of eliminating the errors in depolarisation measurements arising from secondary scattering.

2. *Some Experimental Observations*

In order to eliminate the effect of secondary scattering one has to employ the proper optical arrangement for the measurement of the depolarisation. The correct way of measuring the depolarisation factor is to observe the two components of the scattered track that are separated by the double image prism, in the same background and then to compare their intensities. This method has been designated by Lotmar (1938) as the Cornu method. The defective method of measurement consists in inserting a diaphragm on the observation side, with a very small aperture and thus viewing a portion of the scattered track in a dark background. This method is called the diaphragm method. In this method one measures the combined depolarisation of the primary scattering and of the secondary scattering. Consequently abnormally high values are obtained for ρ_u, ρ_v and ρ_h. The high value of ρ_h obtained by Mookerjee (1938) for phenol-water mixture and the abnormal values of ρ_u, ρ_v and ρ_h obtained by Rao and Muthuswamy (1936) for some emulsions are partly due to the defective method of measurement employed by these investigators. Lotmar (1938) has made a comparative study of the different methods of measuring the depolarisation factors and has shown that the diaphragm method and the photographic method of measurement always give enhanced values for the depolarisation factors.

As has already been pointed out the intensity of secondary scattering per unit volume of the solution depends on the intensity of primary scattering which in turn depends on the number of particles illuminated by the incident beam. Therefore, in order to reduce the effect of secondary scattering it is necessary to reduce the number of particles illuminated by the incident beam. This can be achieved without diluting the colloidal solution, by using a small cell as container and also a narrow pencil of light for measuring the depolarisation factors. In the ideal case one should illuminate a single colloidal particle and measure the depolarisation of the light scattered by it. But in practice this is not possible. Moreover the following observations will show that this is unnecessary. Table I gives the values of ρ_u, ρ_v and ρ_h obtained with a dilute solution of milk for different sizes of the illuminated volume. Since the vertical depth of track inside the medium was large in those cases which are marked with an asterisk the depolarisation measurements were made with a diaphragm on the observation side. The dimensions of the illuminated volume were varied by inserting a diaphragm with variable aperture in the path of the incident beam. A critical study of the figures given in Table I shows that as one reduces the volume of the milk solution, which is directly illuminated by the incident beam the depolarisation factors ρ_u, ρ_v and ρ_h decrease in value progressively. They attain steady values for

TABLE I

a in cm.	b in cm.	c in cm.	V in c.c.	ρ_u %	ρ_v %	ρ_h %
*4	1·5	1·5	9	19·45	6	35·3
*4	1	1	4	18·2	4·95	30·
*4	0·5	0·5	1	15·5	3·64	25·3
*1	1·5	1·5	2·25	17·3	4·8	43·8
*1	1	1	1	15·4	4·2	39·
*1	0·5	0·5	0·25	15·2	3·6	30·
4	0·25	0·25	0·25	8·5	0·28	3·9
4	0·15	0·15	0·09	6·9	0·2	3·4
1	0·25	0·25	0·0625	6·2	0·19	3·4
1	0·15	0·15	0·0225	7·3	0·19	3·1

[a = the length of the track inside the colloidal solution, *i.e.*, the width of the containing vessel. b and c are respectively the horizontal width and vertical depth of track inside the medium. V is the volume of the solution actually illuminated by the incident beam. $V = a \times b \times c$.]

V = about 0·1 c.c. Any further reduction in the volume of the solution illuminated does not appreciably affect the values of ρ_u, ρ_v and ρ_h showing thereby that the secondary scattering has little or no influence on the depolarisation factors. The microscopic depolarisation factors, *i.e.*, the depolarisation factors of the primary scattering are given by the limiting values of ρ_u, ρ_v and ρ_h obtained above.

3. Conclusion

From what has been said above it is clear that in order to eliminate the effect of secondary scattering on depolarisation measurements one has to take the following precautions :—(1) The incident beam of light should be as narrow as possible so as to reduce the volume of the colloidal solution illuminated to a minimum and (2) Cornu method should be employed for the measurement of the depolarisation factors.

The conclusions detailed above are also applicable to the case of liquid mixtures very near the critical solution temperature at which the scattering

becomes very intense. Table II gives the values of ρ_u, ρ_v and ρ_h obtained with a phenol-water mixture which was kept very near the critical solution temperature, for various values of the volume of the mixture illuminated. It is seen that even after eliminating the effect of secondary scattering by using a very narrow pencil of light for illumination and measuring the depolarisation factors by the Cornu method the value of ρ_h is definitely less than unity showing thereby that real clusters of molecules of size not small compared with the wave-length of the incident light exist in liquid mixtures in the neighbourhood of the critical solution temperature.

TABLE II

a in cm.	*b* in cm.	*c* in cm.	V in c.c.	ρ_u %	ρ_v %	ρ_h %
*4	2	2	16	7·5	3·3	81·6
*4	1·5	1·5	9	6·9	2·8	74·
*4	1	1	4	4·5	1·4	53
*4	0·5	0·5	1	2·0	0·37	53
4	0·3	0·3	0·48	0·77	0·12	22
4	0·2	0·2	0·16	0·62	0·09	16
4	0·15	0·15	0·09	0·62	0·1	18
4	0·07	0·07	0·02	0·6	0·09	16

In all the previous measurements of ρ_u, ρ_v and ρ_h in liquid mixtures, which were reported in the *Proceedings of the Indian Academy of Sciences* (Krishnan, 1935, 1937) the author had consistently used a very narrow beam of light (of cross-section about 2 mm./2 mm.) and hence the values of ρ_u, ρ_v and ρ_h were not vitiated by the existence of secondary scattering.

Mookerjee (1938) made some measurements of ρ_h in a phenol-water mixture by the diaphragm method employing a wide beam for illuminating the mixture. In such circumstances the secondary scattering will have a preponderating influence and abnormally high values would be obtained not only for ρ_h but also for ρ_u and ρ_v.

In conclusion, the author takes this opportunity to express his grateful thanks to Prof. Sir C. V. Raman for his kind interest and valuable suggestions during the progress of this investigation.

4. Summary

It is pointed out that in emulsions and protein solutions in which the scattering is very intense, the secondary scattering has a marked influence on the depolarisation factors. The values of ρ_u, ρ_v and ρ_h are in general enhanced, due to the presence of secondary scattering in the solution. The effect of secondary scattering on the depolarisation factors could be eliminated by illuminating the colloidal solution by means of a very narrow pencil of light and then measuring the depolarisation factors by the Cornu method.

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A NOTE ON CAPILLARITY AND SUBSOIL WATER-TABLE

By M. Afzal, M.Sc.
AND
V. I. Vaidhianathan, M.A., D.Sc., F.Inst.P., F.A.Sc.
(From the Irrigation Research Institute, Lahore)

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It has been observed in the Punjab, Sind and other provinces that when there has been a slight shower of rain or even a small amount of irrigation over a wide area, some of the wells, especially the shallow ones rise out of all proportion to the amount of rain or irrigation. The observation pipes which have been put in to record water-table also behave similarly. This question had been referred to us many times, but they could not then be explained. Calculations made on the basis of the permeability of the strata could not account for even a small fraction of such a rise.

An experiment has now been carried out in the Irrigation Research Institute, Lahore, which explains this phenomenon.

An iron tank of about four feet in height and three feet in diameter has two side tubes with strainers fitted near the bottom. The tank is then filled with fine sand and water. When the sand has been packed completely,

Fig. 1

the water in the tank is drained off till it stands about half-way in the side tubes, which are about one centimetre in diameter. A photograph of the tank and those of the side tubes with the levels of water in them is shown in Fig. 1.

If the tank is now allowed to remain for a day, the surface of the sand being exposed to the air, the water-level in the side tubes sinks down by ten centimetres. Now experiments had shown that the amount of evaporation from the surface of the sand could not account for a fall in the level of water in the subsoil in the tank for any thing of this order. The fall of level of water in the side tubes was therefore surprising.

About one hundred grams of water was then sprinkled on the surface of the sand when almost instantaneously the water level in the side tubes began to rise and reached about eight centimetres. Now the amount of water sprinkled could only cause a rise of about 0·04 of a centimetre in the tank taking the pore space to be forty per cent. The abnormal rise of the level of water in the side tubes was therefore not indicating what was taking place in the water level in the body of the sand. The experiment thus provided a clue to the explanation of the abnormal behaviour of wells in the field referred to in the beginning of the note.

The reason for the rise of the level in the tube is this. Water is drawn up by capillarity through the fine pores of the sand and when it reaches the surface of the sand it begins to evaporate. A large number of concave menisci are formed in the interstices near the surface and these exert a negative pull. The water in the side tube is thus held down by this pull of the menisci in the sand. As soon as water is sprinkled on the surface of the sand, free surfaces are formed and the concave menisci are flattened, finally of course forming a continuous flat surface of water. The negative pressure decreases and causes the water in the side tubes to rise by a height which is many times that in the main tank. The action in the wells is also similar.

Any process which flattens the concave menisci causes the water in the side tubes to rise, and any process which increases the concavity, such as evaporation or putting dry sand at the top of the wet sand will cause the level in the side tubes to fall. It is not so much the amount of water evaporated or added on the surface which is the guiding factor in the fluctuation of the level in the side tubes as the negative menisci and the consequent change of pressure. The rise in the tube or in a well in the field is thus not an indication of what is really taking place within the subsoil, unless the other factors in the surrounding field are known. It is remarkable that a phenomenon as surface tension should play such an important rôle in subsoil observation.

Three main factors controlling this rise in the tube are (1) the particle size, (2) the height of the free surface of sand above the water in the tank and (3) the surface tension of water. The second factor brings in what is generally known as the moisture content, field capacity and other secondary effects.

The work has only been begun but in view of the bearing of the results on many engineering and agricultural problems we thought it fit to publish this preliminary note.

ULTRASONIC VELOCITY AND THE ADIABATIC COMPRESSIBILITY OF SOME LIQUIDS

By S. Bhagavantam and Ch. V. Joga Rao
(From the Department of Physics, Andhra University, Waltair)

Received March 13, 1939

1. *Introduction*

Numerous papers relating to the determination of ultrasonic velocities in liquids by the method of diffraction of light have recently appeared in the literature and no attempt will be made here to give exhaustive references. Adiabatic compressiblity is an important physical property that may be deduced from a knowledge of the sound velocity in the liquid. It may also be measured directly by applying a static compression and noting the change produced in a known volume of the liquid contained in a suitable type of piezometer. These two methods of obtaining the same physical property are entirely different and relate to different circumstances under which the liquid is compressed. It is thought that it would be of interest to study a few liquids using both these methods and the present paper describes the results obtained in the case of six liquids. Glycerine and cyclohexanol are chosen to represent the class of highly viscous liquids and benzene, carbon tetrachloride, etc., are chosen to represent the class of less viscous liquids.

2. *Experimental*

A single valve (D.O. 24–Mullard) in a Hartley type of circuit is adopted for generating the oscillations. A quartz crystal, the thickness of which is about 2 mm., is used for setting up the ultrasonic waves in the liquid. The fundamental frequency of the crystal is about 1·6 megacycles. The optical arrangements and other details are similar to those already described by other investigators. λ 5460 A.U. of the mercury arc is used as the optical source. A Philip's Heterodyne wavemeter capable of measuring frequencies correct to 0·2% is used for measuring the frequency. For each setting, the frequency of the oscillator is measured afresh as there are small but appreciable variations caused by the small differences in the setting of the condenser, the temperature of the crystal, etc. The adiabatic compressibility is calculated with the help of the formula $\beta_\phi = \frac{1}{V^2\rho}$ where V is the ultrasonic velocity and ρ the density. The latter at the appropriate temperature is obtained from the *International Critical Tables*. The ultrasonic velocities for different frequencies and at different temperatures are also incidentally measured for some liquids. As only the first order diffraction spectra have been observed

in the case of glycerine, measurements could not be taken over other orders. The results are therefore less reliable in this case than in other liquids where several orders of diffraction spectra have been obtained and measured. At the room temperature, glycerine had to be allowed to settle down for over a day in order to obtain clear fringes.

A glass piezometer suitable for studying the adiabatic compressibilities of ordinary as well as moderately viscous liquids has been developed in this laboratory[1] and this apparatus is used in the present investigation for determining directly the adiabatic compressibility. Reference may be made to earlier papers published in these *Proceedings* for a detailed description of this apparatus. The only point that need be mentioned here is that the movement of the mercury pellet is not instantaneous in the case of very viscous liquids and the results are accordingly less reliable. Nevertheless, attempts have been made to take a large number of readings and only the best representative values are included in this paper. Care is taken to use the same sample of liquid in both the experiments and the work is done at the same time and in the same room so that the temperature is nearly the same in both cases. Liquids are purified by distillation and only the middle fraction is employed, for these experiments.

3. *Results*

In Table I, the compressiblity obtained with the help of the piezometer for pressures ranging between 1 and 2 atmospheres is compared with the compressiblity calculated from the ultrasonic velocity at the same temperature for six different liquids.

TABLE I. *Adiabatic Compressibility*

Liquid	Temperature °C.	Density	Frequency in megacycles	Ultrasonic velocity met. sec.	Compressibility from column 5 (per atm. per c.c.) $\times 10^6$	Compressibility from piezometer (per atm. per c.c.) $\times 10^6$
Benzene	27·5	0·8708	4·35	1283	70·7	72·5
Carbon tetrachloride ..	27·5	1·5800	4·35	932	74·0	74·0
Carbon disulphide ..	27·3	1·2530	4·38	1139	62·3	61·7
Cyclohexanol ..	27·8	0·9416	4·38	1459	50·5	50·5
Acetic anhydride ..	30·0	1·0670	4·34	1249	60·9	58·6
Glycerine	28·5	1·2562	4·48	1957	21·1	21·0

[1] N. M. Philip, *Proc. Ind. Acad. Sci.*, 1939, **9**, 109.

In Table II, the ultrasonic velocities in CCl_4 at 27·5° C. for a range of frequencies are given.

TABLE II. *Ultrasonic Velocity in CCl_4 at 27·5° C.*

Frequency in mega-cycles	1·564	4·35	7·20	13·08
Velocity in metres per sec.	931	932	931	933

Tables III and IV show the dependence of the ultrasonic velocity in cyclohexanol and glycerine respectively on temperature. The density at different temperatures is obtained from the *I.C.T.* and the corresponding compressibilities are claculated.

TABLE III. *Ultrasonic Velocity in Cyclohexanol at Different Temperatures*

Temperature °C.	Density	Velocity in metres per sec.	Compressibility (per atm. per c.c.) $\times 10^6$
30	0·9399	1453	51·0
40	0·9324	1432	53·0
50	0·9248	1400	55·9
60	0·9172	1364	59·3
70	0·9096	1307	65·2
80	0·9020	1258	70·9

TABLE IV. *Ultrasonic Velocity in Glycerine at Different Temperatures*

Temperature °C.	Density	Velocity in metres per sec.	Compressibility (per atm. per c.c.) $\times 10^6$
28·5	1·2562	1957	21·1
40	1·2490	1926	21·9
50	1·2426	1895	22·7
60	1·2360	1862	23·6
70	1·2292	1840	24·3

4. Discussion of Results

The following conclusions may be drawn from the results presented in this paper. The adiabatic compressibility of a liquid determined by the method of ultrasonic diffraction agrees very closely with that determined directly by using a piezometer. This result holds good alike for all liquids irrespective of whether they are highly viscous or not. There is no dispersion of the ultrasonic velocity in the range 1 to 13 megacycles for carbon tetrachloride. Similar results obtained in certain liquids have already been published by other workers.[2] The absolute value obtained for the ultrasonic velocity in CCl_4 is however distinctly higher than the one recently published by Seifen.[3] Viscous liquids do not exhibit any abnormal temperature coefficient of the sound velocity at moderate temperatures. The gradient is about $-3{\cdot}0$ metres per sec. per degree and is more or less the same as that exhibited by the less viscous liquids like toluene and carbon tetrachloride.

5. Summary

The ultrasonic velocity has been measured in benzene, carbon tetrachloride, carbon disulphide, cyclohexanol, acetic anhydride and glycerine and hence the adiabatic compressibility calculated. The latter has also been measured directly with a piezometer and good agreement is found to exist between the values obtained in the two methods for all the six liquids. No dispersion of the ultrasonic velocity has been found in carbon tetrachloride in the range 1 to 13 megacycles. The dependence of the ultrasonic velocity on temperature has been investigated in cyclohexanol and glycerine in the range 30° C. to 80° C.

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[2] R. Bär, *Proc. Ind. Acad. Sci.*, 1938, **8**, 289.
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A SPECIAL NET OF QUADRICS

By B. Ramamurti
(*Annamalai University, India*)

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The special net of quadrics obtained by taking the polar quadrics of the points of a plane with regard to a cubic surface has been studied by Schur Töplitz, Dixon and recently by W. L. Edge.[1] It is known that such a net is also a polar net of ∞^2 cubic surfaces with respect to the points of a suitably chosen osculating plane of a twisted cubic R^3. The Sylvester pentahedra of the ∞^2 cubic surfaces form a pencil circumscribed to R^3, each pentahedron corresponding to ∞^1 cubic surfaces. Conversely, as pointed out by Edge, a pencil of circumscribed pentahedra of R^3, uniquely determines the polar net of quadrics, which can be directly defined as the net for which the pentahedra are self-polar. This point of view leads him to the generalisation that there is a unique net of quadrics in $[n]$ for which a pencil of $(n+2)$-hedra circumscribed to a rational norm curve R^n are self-polar[2] and to a study of such a net.

The object of this paper is, first of all, to prove the generalisation of Edge by the method of binary apolarity, and then study the special net of quadrics in [3] by taking up his point of view. The method adopted has the advantage of providing a binary invariant specification with respect to R^3 of the net of quadrics and the associated cubic surfaces. It is shown that the cubic surfaces are determined in a (1, 1) manner by binary forms a_x^9 having a given form b_x^8 as a first polar. The investigation of such forms and their representation in [9], by the author in a previous paper[3] leads to the important result that the ∞^2 cubic surfaces can be represented in a (1, 1)

[1] Schur, *Math. Annalen*, **18**, 23–27.
Töplitz, *ibid.*, **10**, 434–63.
Dixon, *Proc. London Math. Soc.*, **2**, 7, 150–56.
W. L. Edge, *Proc. Edinburgh Math. Soc.*, 1936, **4**, 185–207. I am indebted to this paper for the references cited above.

[2] A $(n+2)$-hedron formed by $(n+2)$ primes is said to be self-polar with respect to a quadric, when the polar primes of the point of intersection of any n prime faces contains the $(n-2)$ common to the other two.

[3] Ramamurti, "On rational normal ruled surfaces," *Mathematische Annalen*, 1935, 582–86. In this paper the general case of forms a_x^n having a given b_x^{n-1} as a first polar is taken up.

manner by the points of a rational normal ruled surface V_2^8 in [9]. This determination of the exact structure of the system enables us to explain the difficulty of Edge regarding the discrepancy between his value 14 and the value 18 of Töplitz obtained for the degree of one of the two parameters in the equation of system of cubic surfaces.[4] It is shown here that the different values are due to the different " Abbildungen " of V_2^8 on a plane and that the lowest value, which corresponds to the " Minimal Abbildung " of V_2^8 is 4.

1. The basis of our proof for the generalisation of Edge is to be found in the following fact in binary forms.

Given a pencil of binary (n + 2)*-ics* $g_1^{n+2} = a_x^{n+2} + k\beta_x^{n+2}$ *there is a net of* 2n*-ics apolar to it, these being the second polars of the unique apolar* (2n + 2)*-ic.* (1.1).

The apolarity of a form of order $(2n + 2)$ to another of order $(n + 2)$ involves $(n + 1)$ conditions linear in the coefficients of each. Hence there is a unique form b_x^{2n+2} apolar to a_x^{n+2} and β_x^{n+2} and hence to every member of the pencil g_1^{n+2}. Similarly there must be a net of $2n$-ics apolar to g_1^{n+2}. Since b_x^{n+2} is apolar to it, its second polars are also apolar to it, and hence constitute the apolar net of $2n$-ics.

Let us regard a rational norm curve R^n in $[n]$ as the carrier of a binary variable x. Let $a_x^{n+2} = 0$ and $\beta_x^{n+2} = 0$ give parametrically the points of contact with R^n of the prime faces of any two $(n + 2)$-hedra circumscribed to R^n. Hereafter we denote the $(n + 2)$-hedra by P (a_x^{n+2}) and P (β_x^{n+2}) respectively. Let Q (A_x^{2n}) denote the unique quadric cutting R^n at the points A_x^{2n} and outpolar to R^n.[5] We shall now prove

Any quadric Q with respect to which P (a_x^{n+2}) *is self-polar must be an outpolar quadric determined by a binary form* A_x^{2n} *apolar to* a_x^{n+2}*, and conversely.* (1.2).

Let $a_x^{n+2} = a_{1x}\ a_{2x}\ a_{n+2,x}$. If π_r denotes the osculating prime of R^n at the point a_{rx}, any quadric Q for which P (a_x^{n+2}) is self-polar must be of the form

$$\sum_1^{n+2} A_r\, \pi_r^2 = 0 \qquad (1.3)$$

The degenerate quadrics π_r^2 are outploar quadrics determined by the perfect $2n$-th powers a_{rx}^{2n}. Hence Q also must be an outpolar quadric determined by the $2n$-ic

$$A_x^{2n} = \sum_1^{n+1} A_r\, a_{rx}^{2n}. \qquad (1.4)$$

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[4] W. L. Edge, *loc. cit.*, foot-note 1, p. 187.

[5] A quadric is said to be outpolar to R^n if it is outpolar to all the quadric envelopes circumscribed to R^n.

Each of the forms $a_{rx}{}^{2n}$ is a polar to $a_x{}^{2n}$ and hence $A_x{}^{2n}$ is also apolar to it. Conversely if $A_x{}^{2n}$ is apolar to $a_x{}^{n+2}$, it is well-known that it can be expressed in the form (1.4) and hence $Q(A_x{}^{2n})$ in the form (1.3), so that the $(n+2)$ hedron $P(a_x{}^{n+2})$ is self-polar with respect to it.

From (1.1) we have a net of $2n$-ics apolar to $g_1{}^{n+2}$, and hence from (1·2) we have

THEOREM 1. *Given a pencil of* $(n+2)$*-hedra circumscribed to a rational norm curve* R^n *in* $[n]$, *there is a net of quadrics for which they are self-polar. If the* $(n+2)$*-hedra are given parametrically by* $a_x{}^{n+2} + k\beta_x{}^{n+2}$, *and if* $b_x{}^{2n+2}$ *be the unique apolar* $(2n+2)$*-ic, the net of quadrics is the net of outpolar quadrics determined by the* $2n$*-ics which are the second polars of* $b_x{}^{2n+2}$.

The first part of Theorem 1 is the generalisation of Edge[6] and the second part gives an invariant specification of the net of quadrics.

2. From Theorem 1 we have in particular in [3] the following :

THEOREM 2. *Given a pencil of pentahedra circumscribed to a twisted cubic* R^3, *the quadrics for which they are self-polar form a net. If the pencil of pentahedra be given parametrically by* $a_x{}^5 + k\beta_x{}^5$, *and* $b_x{}^8$ *be the unique apolar octic, the net of quadrics is the net of out-polar quadrics determined by the second polar of* $b_x{}^8$. Let us hereafter refer to this net as $N(b_x{}^8)$. We will now show that it is the polar net of ∞^2 cubic surfaces, and obtain a specification for the system of cubic surfaces : It is well known that given a binary form $a_x{}^9$, there is a unique cubic surface $C(a_x{}^9)$ cutting R^3 at the points given parametrically by $a_x{}^9$ and outpolar to R^3, *i.e.*, the polar quadrics of C are outpolar to R^3[7]. Also if $\lambda_1, \lambda_2, \lambda_3$ are the parameters of the points of contact of the osculating planes of R^3 which pass through a point A, the polar quadric of C with respect to A is the outpolar quadric determined by the sextic $a_x{}^6\, a_{\lambda 1}\, a_{\lambda 2}\, a_{\lambda 3}$. Hence the polar quadrics of $C(a_x{}^9)$ with respect to the points in the osculating plane at the point λ of R^3 form the net of outpolar quadrics determined by the second polars of $a_x{}^8\, a_\lambda$. So if $a_x{}^8\, a_\lambda \equiv b_x{}^8$, this net is identical with $N(b_x{}^8)$, so that $N(b_x{}^8)$ is a polar net of the cubic surface $C(a_x{}^9)$ with respect to the points in the osculating plane at the point λ. There are ∞^2 forms $a_x{}^9$ having a given form $b_x{}^8$ as a first polar, and these then correspond to the cubic surfaces for which $N(b_x{}^8)$ is a polar net. Thus we have

THEOREM 3. *The net of quadrics* $N(b_x{}^8)$ *is a polar net of the* ∞^2 *cubic surfaces outpolar to* R^3 *and determined by the* ∞^2 *forms* $a_x{}^9$ *having* $b_x{}^8$ *as a first*

---

[6] W. L. Edge first proves that there is a unique net of quadrics for which two circumscribed $(n+2)$-hedra of R^n are self-polar, and then shows that the same net is obtained by taking any two $(n+2)$-hedra.

[7] Meyer, *Apolarität und Rationale Curven*, page 370.

polar. If $a_x^8\ a_\lambda \equiv b_x^8$, *the plane associated with the cubic surface* C (a_x^9) *is the osculating plane of* R^3 *at the point of* λ.

The forms a_x^9 having b_x^8 as a first polar, and more generally the forms a_x^n having a given b_x^{n-1} as a first polar has been investigated previously by the author and the main result which is relevant to us, is the following geometric representation in $[n]$.

If binary forms of order n are represented by the points of a $[n]$ with reference to a rational norm curve R^n in it the forms a_x^n having a given b_x^{n-1} as a first polar correspond to the points of a rational normal ruled surface V_2^{n-1} on which R^n is a leit-curve, *i.e.*, a curve intersecting every generator of V_2^{n-1} at a single point. Further the generator of V_2^{n-1} through the point λ of R^n corresponds to forms whose first polar with respect to λ are identical with b_x^{n-1}.[8]

Taking the case $n = 9$, and remembering that to every form a_x^9 having b_x^8 as a first polar corresponds a cubic surface for which N (b_x^8) is a polar net, we have

THEOREM 4. *The* ∞^2 *cubic surfaces for which* N (b_x^8) *is a polar net can be represented in a one-one manner by the points of a rational normal ruled surface* V_2^8 *in* [9]. *The generators of* V_2^8 *correspond to the pencils of cubic surfaces associated with the same osculating plane of* R^3.

Let us now specify the Sylvester pentahedra of the cubic surfaces. It is well known that if γ_x^5 be the unique apolar quintic of a_x^9, the pentahedron P (γ_x^5) is the Sylvester pentahedron of the cubic surface C (a_x^9). In our case $a_x^8\ a_\lambda \equiv b_x^8$. Hence γ_x^5 must be apolar to b_x^8 and hence must belong to the apolar pencil g_1^5. Conversely given a member γ_x^5 of g_1^5, the cubic surfaces having P (γ_x^5) as the Sylvester pentahedron, correspond to forms apolar to γ_x^5 and having b_x^8 as a first polar. Hence in the representation in [9] they correspond to the section of V_2^8 by the chordal [4] of R^9 cutting it at the points γ_x^5. This section is known to be a minimal leit-curve of V_2^8, a rational norm curve R^4 of order 4.[9] In fact the α' minimal leit curves of V_2^8 are given by the chordal [4]'s is of R^9 corresponding to the pencil g_1^5. Thus we have

THEOREM 5. *In the representation of the* ∞^2 *cubic surfaces by the points of a* V_2^8 *in* [9], *the* ∞^1 *minimal leit-curves of* V_2^8 *correspond to the* ∞^1 *systems of cubic surfaces with the same Sylvester pentahedron.*

Since every generator V_2^8, intersects a minimal leit-curve at a single point, it follows that given the Sylvester pentahedron and an osculating plane λ of R^3, there is a unique cubic surface.

[8] Ramamurti, *loc. cit.*, Theorem 1.

[9] Ramamurti, *loc. cit.*, Theorem 3.

3. We shall now obtain the equation of the system of cubic surfaces. If we take the corresponding V_2^8, the points on the minimal leit-curve $\propto (a_x^5)$ correspond to forms a_x^9 apolar to a_x^5 and having b_x^8 as a first polar.

Let $$a_x^5 \equiv a_{1x}\, a_{2x}\, a_{5x}.$$

Since b_x^8 and a_x^9 are both apolar to a_x^5

$$b_x^8 \equiv \sum_1^5 A_r\, a_{rx}^8$$

$$a_x^9 \equiv \sum_1^5 A_r'\, a_{rx}^9$$

Since $$a_x^8\, a_\lambda \equiv b_x^8$$

$$A_r' = \frac{A_r}{a_{r\lambda}}.$$

Hence a_x^9, on being multiplied by a_λ^5 becomes

$$a_\lambda^5 \sum \frac{A_r\, a_{rx}^9}{a_{r\lambda}} \qquad (3\cdot1)$$

Thus (3·1) gives any point on the leit-curve $\propto (a_x^5)$.

Similarly the curve $\propto (\beta_x^5)$ can be represented parametrically by

$$\beta_\lambda^5 \sum \frac{B_r\, \beta_{rx}^9}{\beta_{r\lambda}} \qquad (3.2)$$

where $$\beta_x^5 = \beta_{1n}\, \beta_{2n}\, \beta_{5x}$$

$$b_x^8 = \sum B_r\, \beta_{rx}^8$$

The generator V_2^8 connecting the points λ of the two leit-curves $\propto (a_x^5)$ and $\propto (\beta_x^5)$ is then

$$a_\lambda^5 \sum_1^5 \frac{A_r\, a_{rx}^9}{a_{r\lambda}} + \mu.\ \beta_\lambda^5 \sum_1^5 \frac{B_r\, \beta_{rx}^9}{\beta_{r\lambda}} \qquad (3.3)$$

In (3.3) if λ is constant and μ varies, we get a generator of V_2^8, while if μ is constant and λ varies we get a minimal leit-curve of V_2^8. Thus (3.3) gives a representation in terms of the two parameters λ and μ of any point of V_2^8 or equivalently of any form a_x^9 having b_x^8 as a first polar.

If π_r, π_r' denote respectively the osculating planes of R^3 at the points a_{rx} and β_{rx}, π_r^3, $\pi_r'^3$ are the outpolar cubic surfaces corresponding to the forms a_{rx}^9 and β_{rx}^9 the required equation of the ∞^2 cubic surfaces corresponding to the forms of order 9 given in (3.3) is

$$a_\lambda^5 \sum_1^5 \frac{A_r\, \pi_r^3}{a_{r\lambda}} + \mu\, \beta_\lambda^5 \sum \frac{B_r\, \pi_r'^3}{\beta_{r\lambda}} = 0 \qquad (3.4)$$

In the above equation one of the parameters μ is linear while the other λ is of degree 4. In the equation of the same system obtained by Edge, one is linear, but the other is of degree 14. Edge further observes that according

to Töplitz it is 18, and remarks that he is unable to explain the discrepancy, between the two values.[10] We shall now give an explanation of the different values, and show that these and other values are also possible, and that the lowest value is 4.

The explanation is to be found in the following general observation. Consider a system of ∞^2 surfaces $f(x\ y\ z\ \lambda\ \mu) = 0$ any member of which can be expressed rationally in terms of the two parameters λ and μ. Let λ, μ be of degree k and l respectively. Suppose further that to each member corresponds a unique set of values of λ, μ, and that every member of the system can be expressed linearly in terms of $(n+1)$ fixed members of the system so that $f(x\ y\ z\ \lambda\ \mu) \equiv \sum_0^n \phi(x\ y\ z)\, f_r(\lambda, \mu)$.

Then the system can be represented in a one-one manner by the points of a rational surface V_2 in $[n]$ given by

$$\xi_r = f_r(\lambda, \mu) \qquad r = 0, 1, n$$

Any point on V_2 can be mapped uniquely by the point (λ, μ) in a plane. The prime sections of V_2 correspond to the system of curves

$$\Sigma A_r f_r(\lambda, \mu) = 0 \text{ of degree } k + l.$$

Now we may take any Cremona transformation in the plane carrying the point (λ, μ) to the point $\lambda'\ \mu'$, and $\lambda'\ \mu'$ may as well be taken to be the parameters. But in a Cremona transformation the order of a system of curves may change and consequently the values k and l, so that k and l are not numerical invariants of the system, and may vary with different representations. But it is known that there is a lowest value to which the order of the system of curves may be reduced by a Cremona transformation, and the representation by the new parameters $\lambda'\ \mu'$ is then the 'Minimal Abbildung' of V_2.[11]

In our case the ∞^2 cubic surfaces are represented by the points of a rational normal surface V_2^8 in $[9]$. There are leit-curves of various orders on it from the lowest value 4 to the highest 9 and the different representations of V_2^8 are obtained by taking leit-curves of different orders on it. Thus if we take two leit-curves of order r and if the points of intersection of the two curves with any generator has the same parameter λ, then any point of V_2^8 can be expressed parametrically in the form

$$x_\iota = f_\iota(\lambda) + \mu\, \phi_\iota(\lambda) \qquad \iota = 0, 1, 9$$

where the f's and ϕ's are polynomials of order r. In this case while one parameter μ is linear the other is of degree r. In the minimal representation

[10] W. L. Edge, *loc. cit.*, foot-note 1, p. 187.

[11] Bertini, *Mehrdimensionaler Raume*, p. 344, foot-note 8.

which is obtained by taking two minimal leit-curves the second parameter is of degree 4, and is the lowest value. It can be easily seen that the equation of Edge corresponds to taking a minimal leit-curve, and another leit-curve of order 9. But then he gets the second parameter to be 14. This could be reduced to 9, by the simple Cremona transformation

$$\alpha' = \alpha$$
$$\lambda' = \lambda (\alpha - \theta_1)(\alpha - \theta_2)(\alpha - \theta_3)(\alpha - \theta_4)(\alpha - \theta_5)$$[12]

Similarly the degree 18 of Töplitz can be explained.[13]

[12] Bertini, *loc. cit.*

[13] W. L. Edge, *loc. cit.*, Equation given in page 186.

THE SPACE ARRANGEMENTS OF ATOMS—PART I

The Configuration of Nitrogen in the 3-Covalent State

By Bawa Kartar Singh

(From the Chemical Laboratories, Science College, Patna)

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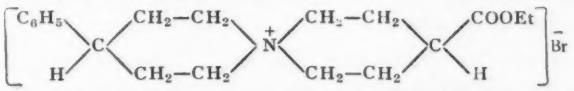
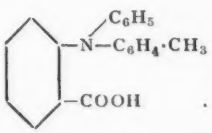
Even as early as 1877, Wislicenus suggested that Van't Hoff's theory of stereoisomerism in carbon compounds might be extended to quaternary ammonium salts. Since then a great deal of experimental data has been forthcoming to enable us to establish the configuration of the ammonium ion. The brilliant investigation of Mills and Warren[1] in which they resolved 4-phenyl-4′-carbethoxy-bispiperidinium 1,1′-spirane bromide, has established



beyond any doubt that the four groups covalently linked to nitrogen are arranged tetrahedrally round the nitrogen atom, just as are the four groups attached to the carbon atom in a derivative of methane.

The molecular configuration of the other type of nitrogen compounds, with 3-covalent nitrogen atom as in ammonia (NH_3), or an amine (Nabc), having a valency group of 8 electrons, of which 6 are shared, remained for long as one of the outstanding problems of stereochemistry. Krafft,[2] Behrend and König[3], Ladenburg[4], Fischer[5], and Jones[6] made attempts under different conditions to resolve tervalent nitrogen compounds, in which the nitrogen atom was linked to 3 different groups. All such attempts ended in failure. The latest of these unsuccessful attempts was that of Meisenheimer,[7] who prepared the triarylamine, N-phenyl, N-*p*-tolyl anthranilic acid,

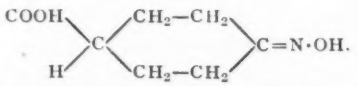


The nitrogen atom in this compound is non-basic, so that no complications are introduced by a change of valency of the nitrogen during the process of resolution with the aid of optically active bases. The conclusion

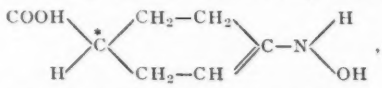
which may be drawn from these negative experiments is that the nitrogen atom lies in one plane with the three attached groups, so that the molecule possesses a plane of symmetry. It is, however, admitted that conclusions drawn from negative evidence are not of much value. Moreover evidence from the study of certain physical properties points to the other alternative, namely, that the nitrogen atom does not lie in one plane with the three attached groups, so that the molecule is pyramidal in shape. The value of the electric moment of ammonia,[8] 1·5 indicates that its molecule does not possess a centre of symmetry. The evidence from the absorption spectrum of ammonia in the infra-red is even more strong (Badger and Mecke[9]). The crystal structure of solid ammonia also indicates that its molecular configuration is pyramidal (Mark and Pohland[10]).

There is yet another kind of evidence, according to which the distribution of three valencies in tervalent nitrogen compounds of the ammonia and the amine types is non-planar. The object of this paper is to bring forward this evidence, deduced from stereochemical considerations and based on conclusive experimental data.

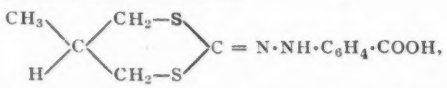
The non-planar configuration of the doubly linked tervalent nitrogen atom called for by the Hantzsch and Werner's theroy of the configuration of the oximes has been established by W. H. Mills and his co-workers. Mills and Bain[11] prepared and resolved the oxime of *cyclo*hexanone-4-carboxylic acid :



In order to remove any objection that the compound may not have the structure allotted to it, but may be the isomeric *cyclo*-hexenyl hydroxylamine,

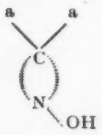


in which the carbon atom marked with an asterisk is asymmetric, and its enantiomorphism has nothing to do with the configuration of the nitrogen atom, Mills and Saunders[12] prepared and resolved *O*-carboxyphenyl hydrazone of methyltrimethylene dithiocarbonate,



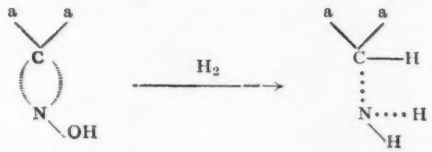
into its optically active components. The hypothesis of Hantzsch and Werner implies a certain space configuration of the oximino group, and the existence of these compounds in enantiomorphous forms is only possible, if

the assumptions underlying the hypothesis are true. These brilliant investigations of Mills prove conclusively that the doubly linked valencies of nitrogen in the oxime grouping are not co-planar with the singly linked one, thus :



This result, based on crucial experimental facts, can be made use of to deduce the arrangement of the three groups attached to a trivalent nitrogen atom, as in an amine Nabc, in the following way :

On reduction, an oxime is converted into an amine, according to the scheme :



(I) (II)

The doubly linked valencies of nitrogen (shown by dotted lines), in the oxime (I), lie in a plane, which does not contain the singly linked valency (firm line), carrying the hydroxyl group. In the amine (II), the two single valencies of nitrogen (dotted lines), resulting from the doubly linked valencies of the oximino group (I), still lie in the same plane ; the third valency (firm line), to which is attached a hydrogen atom and which originally carried the hydroxyl group in the oxime (I), lies outside this plane.* In other words, the three valencies of the nitrogen atom in an amine lie in two different planes.

Stereochemical formulæ are best visualised from concrete models : Fig. 1 represents the photograph of the model of an oxime ; one of the two large spheres represents the carbon atom and the other the nitrogen (striped), to which a smaller sphere representing the oxygen atom is attached ; the latter carries a still smaller sphere, representing the hydrogen atom. It is clearly shown that the link (striped), carrying the spheres representing the hydroxyl group, does not lie in the plane which contains the two links representing the double bond. Fig. 2 represents the photograph of the model

* If in the molecule of the oxime, under consideration, the plane containing the doubly linked valencies of nitrogen does not *originally* contain the singly linked valency carrying the hydroxyl group, the position of the latter linkage will remain unaltered relatively to this plane after the replacement of the doubly linked valencies by two single valencies in the resulting amine.

of the corresponding amine. The same notation applies to the different spheres in Figs. 1 and 2. The double link, between the spheres representing

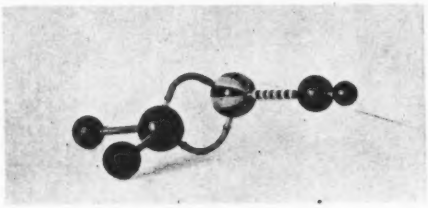


FIG. 1

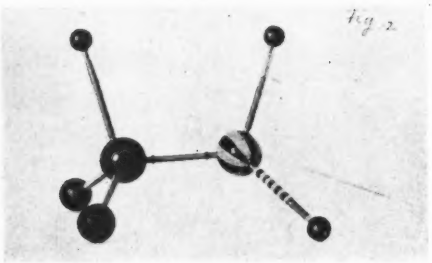


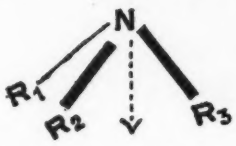
FIG. 2

nitrogen and carbon atoms (Fig. 1) is replaced by two single links, one of them joining these two spheres, and the second link carrying a smaller sphere, representing the hydrogen atom. These two single links, attached to the nirogen sphere, are in the same plane. The remaining third link (striped), which carries a smaller sphere, representing the hydrogen atom, does not lie in this plane.

It is thus proved that the three valencies of nitrogen in tervalent nitrogen compounds of the amine or ammonia type are not coplanar. The deduction is simple : it is based on stereochemical considerations, supported by unimpeachable experimental evidence. It finds support also from physical properties, such as the electric moment, crystal structure, and absorption spectra in the infra-red, which are correlated with the space arrangement of the molecule.

In view of the space configuration of the tervalent nitrogen deduced above, a tertiary amine with three different groups attached to the nitrogen atom, must be an enantiomorphous arrangement, and such compounds should be capable of resolution into their optically active components. As already mentioned, this has never been realised experimentally, these compounds having defied all attempts at resolution. The failure to demonstrate

optical activity when the three radicals are different is evidently due to the ease with which the nitrogen nucleus can pass backwards and forwards



(1)

(2)

between the positions (1) and (2), resulting in the rapid racemisation of this class of compounds, even at the ordinary temperature.

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CONSTITUTION OF NARINGIN

The Position of the Sugar Group

By S. Rangaswami, T. R. Seshadri
and
J. Veeraraghaviah
(From the Departments of Chemistry and Chemical Technology, Andhra University, Waltair)

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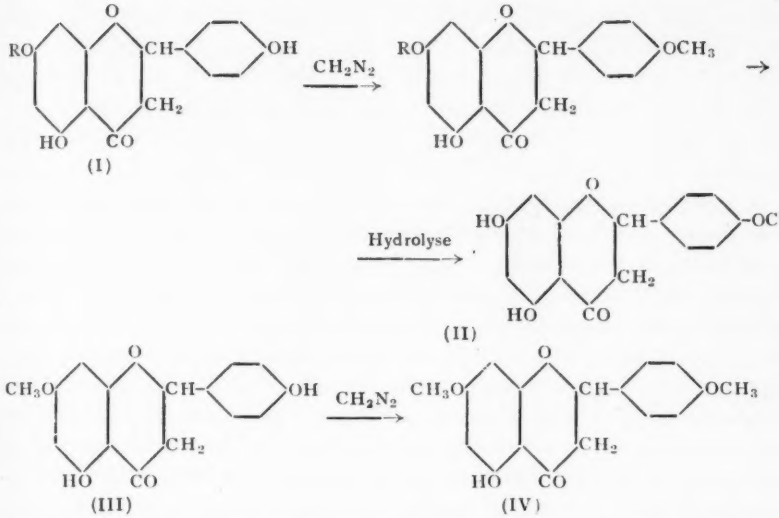
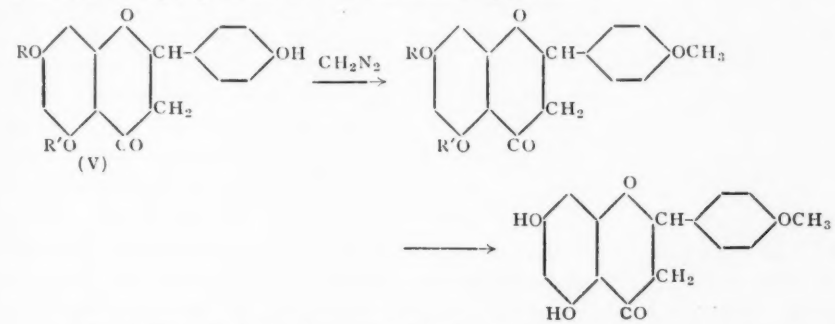
The crystalline bitter principle, naringin was first isolated in 1866 by de Vry in Java from grape fruit blossoms. Recently it has been produced in large quantities from grape fruit residues. In the course of our work on the chemistry of Indian fruits we have prepared naringin from the peels and rags of the pamparapanas fruit (*Citrus paradisi*). When anhydrous the substance has the composition $C_{27}H_{32}O_{14}$ and on hydrolysis with acids gives rise to an aglucone called naringenin along with a molecule of glucose and a molecule of rhamnose. Naringenin has the formula $C_{15}H_{12}O_5$. Though at first it was thought to be a chalkone[1] it was finally proved to have the constitution of 5 : 7 : 4′-trihydroxyflavanone (I, R = H) by Asahina and Inubuse[2] in 1928. This was confirmed subsequently by its synthesis by Shinoda and Sato[3] by condensing phloroglucinol with the ethyl carbonate of *p*-coumaric acid in the presence of aluminium chloride.

An attempt was made by Asahina and Inubuse[4] to locate the position of the sugars in the molecule of naringin. On heating the substance with barium hydroxide for 12 hours in an atmosphere of hydrogen it was found to yield *p*-hydroxy-benzaldehyde and a glycoside of phloracetophenone. The latter on further hydrolysis with dilute sulphuric acid yielded phloracetophenone, glucose and rhamnose. By the action of diazomethane on naringin a syrupy substance was obtained which on hydrolysis gave a monomethyl ether of naringenin known as *iso*-sakuranetin (II). It was therefore clear that the sugar residues were present in the benzopyrone portion of the molecule. Though there was no definite experimental evidence that they existed as a disaccharose unit, Asahina and Inubuse made this assumption from general considerations and concluded that the rhamnoglucose unit was present in position 7. Since it was known that position 5 is resistant to methylation under these conditions the formation of *iso*-sakuranetin was explained according to the scheme given below (R = sugar group) :



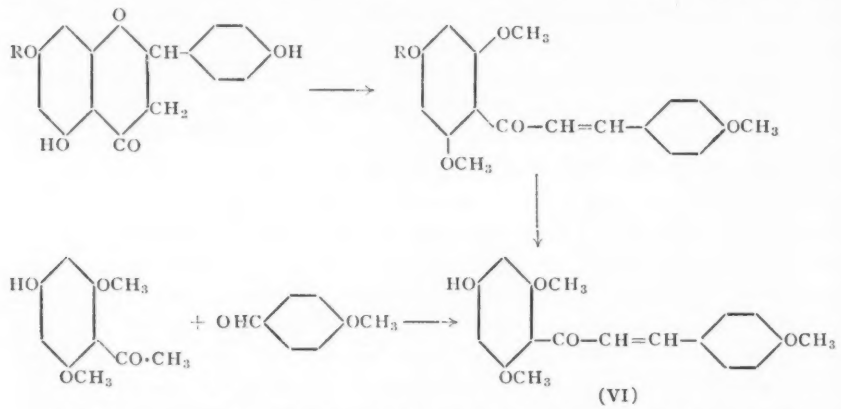
In this connection the similarity between naringin and sakuranetin (III) is noteworthy, since the latter undergoes monomethylation in position 4′ only to give 4′ : 7-dimethyl ether of naringenin (IV). But the experimental results of Asahina and Inubuse could equally satisfactorily be explained if two monosaccharose units should occupy positions 5 and 7 in naringin as in (V). The indefiniteness of the above results was due to the fact that the reagent diazomethane is not capable of methylating all the free phenolic hydroxyl groups present in the flavanone glycoside.



With a view to definitely establish the final constitution of naringin a successful attempt has now been made to methylate it completely using methyl iodide and potassium carbonate in acetone medium. It was found by King and Robertson[5] that hesperidin which is a glycoside of the flavanone

hesperitin underwent complete methylation of the phenolic hydroxyl groups under these conditions though many of the hydroxyl groups of the sugar portion remained unaffected. At the same time the flavanone ring had opened out to form the corresponding chalkone. On the other hand, Lal[6] noticed in connection with butrin that the opening of the pyrone ring took place only partially giving rise to two methylated products.

On methylating naringin by the above method and hydrolysing the product using alcoholic hydrochloric acid a brown solid was obtained which after repeated purification yielded a pale yellow crystalline compound melting at 206–7°. It was homogeneous and did not produce a red colour on reduction with magnesium and hydrochloric acid showing thereby the absence of the pyrone ring.[7,8] Hence it was obvious that the pyrone ring had opened out completely during the methylation. The final product had the composition $C_{18}H_{18}O_5$ and contained three methoxyl groups. Its identity with 2 : 6 : 4′-trimethoxy-4-hydroxychalkone (VI) was proved by comparison with a synthetic sample of the chalkone. For this synthesis 2 : 6-O-dimethyl-phloroacetophenone prepared according to the method of Canter *et al.*,[9] was condensed with anisaldehyde by the improved procedure recently described by Nadkarni and Wheeler.[10] The transformations are represented below:



(VI)

As a consequence of these experiments it is definitely established that in naringin there exists a disaccharide grouping attached to position 7 (Formula I, R = $C_{12}H_{21}O_9$). In this respect it is similar to the related compound hesperidin.

Experimental

Methylation of Naringin and Preparation of 2 : 6 : 4′-*Trimethoxy-4-hydroxy-chalkone.*—A suspension of naringin (5 g.) and anhydrous potassium carbonate

(5 g.) in a mixture of dry acetone (100 c.c.) and methyl iodide (10 c.c.) was heated under reflux on a water-bath. At the end of 30 hours further quantities of methyl iodide (10 c.c.) and potassium carbonate (5 g.) were added and the heating continued for another 30 hours. After cooling, the solution was filtered from inorganic salts and evaporated in a vacuum. A brown syrup was obtained and this was hydrolysed by refluxing with about 80 c.c. of alcoholic hydrochloric acid containing 5% of hydrogen chloride for 2 hours. The mixture was cooled, diluted with water (500 c.c.) and set aside. The brown precipitate which separated was filtered on the following day and washed several times with water. On repeated crystallisation from ethyl alcohol pale yellow glistening micacious plates of the chalkone melting at 206° to 207° were obtained. (Found: C, 68·9; H 6·1; $-OCH_3$ 29·1; $C_{18}H_{18}O_5$ requires C 68·8; H 5·7; $-OCH_3$ 29·6%.) It did not produce a red colour with a reducing mixture of magnesium and hydrochloric acid thereby showing the absence of any flavanone structure. It was moderately soluble in pure alcohol and rather sparingly in 50% alcohol and the alcoholic solution did not give any characteristic colour with ferric chloride or lead acetate. It was readily soluble in cold dilute alkali giving a yellow solution from which it was re-precipitated on the addition of acids. A mixed melting point with the sample syntbesised as below showed them to be identical.

2 : 6-0-*Dimethyl-phloracetophenone* was prepared from phloracetophenone by the method of Canter *et al.* (*loc. cit.*) It crystallised from methyl alcohol in slender prisms melting at 186° to 187°.

Synthesis of 2 : 6 : 4′-*Trimethoxy*-4-*hydroxychalkone*.—A solution of the above ketone (0·5 g.) and anisaldehyde (0·5 g.) in alcohol (3 c.c.) was treated at 0° with an ice-cold solution of potassium hydroxide (5 g. in 4 c.c. of water) and left out of contact with air for 4 days with occasional shaking. The mixture was then diluted with water (15 c.c.) and acidified with dilute hydrochloric acid, the temperature being maintained below 5°. A yellow solid separated which after filtration and washing with water was crystallised from aqueous alcohol (yield almost quantitative). A small quantity of a grey powder which was less soluble than the main portion was rejected. A repetition of the crystallisation gave the chalkone as pale yellow needles and micacious plates melting at 204° to 205° (mixed m.p. 205° to 207°) and possessing all the properties of the sample prepared from naringin. (Found: OCH_3 26·2, loss on drying at 140°, 10 ·0; $C_{18}H_{18}O_5,2H_2O$ requires $-OCH_3$ 26·6, loss on drying 10·3%. Found in the dehydrated specimen: C 68·9; H 6·0 $C_{18}H_{18}O_5$ requires C 68·8, H 5·7%.) The sample had a tendency to lose its water of hydration on crystallisation from anhydrous alcohol.

Summary

Methylation of naringin by means of methyl iodide and potassium carbonate in acetone medium opens out the pyrone ring and methylates all the phenolic hydroxyl groups. The product on hydrolysis yields 2 : 6 : 4′-trimethoxy-4-hydroxychalkone. It is therefore concluded that in naringin the sugars, glucose and rhamnose exist as a disaccharide unit attached to position 7.

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SCATTERING OF LIGHT BY LARGE WATER DROPS—PART I

By G. R. Paranjpe, V. G. Naik and P. B. Vaidya

(From the Department of Physics, Royal Institute of Science, Bombay)

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Historical

The theory of the scattering of light has been worked out on the basis of Maxwell's electromagnetic theory of light by Rayleigh[1], Love[2], Mie[3] and many others[4]. Reyleigh[1] has treated the theory in different aspects, *viz.*, (i) for dielectric spheres, whose dimensions are small as compared to the wave-length of light, (ii) for spheres with radii comparable to the wave-length of light, (iii) for large spheres whose refractive index is small, and (iv) for spheres of any size and any refractive index. Most of the workers in the field have, however, limited their investigations to the first two groups only. Comparatively little data are available for the third case. The last case has been worked out mainly by Love[2]. Mie[3] has worked out a general theory nearly on the same lines as Love without any restriction as to the refractive index or the size of the particles. The only assumption made was that the scattering particles were spherical. The theory of Mie has been mostly used in modified form by Debye[5], Ganz[6], Mecke[7], and others to study the phenomenon of scattering. In spite of these modifications the theoretical study, as also the experimental one, of the changes, which would occur as the scattering spheres become large as compared to the wave-length of light, remains still to be fully investigated. The calculations of the scattering functions for larger drops become very lengthy and are such that any slip of a small magnitude or of a sign would entirely change the nature of the results.

Blumer[8] was the first to work out elaborately the nature of the scattering curves by particles of different sizes and of different refractive indices on the basis of Mie's theory. His calculations are restricted to a maximum radius of sphere of about $0{\cdot}3\ \mu$ in the case of water. Rayleigh[1] made theoretical calcultions for particles comparable to the wave-length of light. B. Ray[9] extented the calculations by using Rayleigh-Love theory to particles with radii nearly double the wave-length of light and used these to explain the change of axial colours as seen in sulphur suspensions in water. Blumer[8] examined later on various theories of scattering from the stand-point of Mie's theory and pointed out certain limitations and corrections necessary to the approximate theories of Wiener[10], Lambert[11] and Lommel and Seeliger[12].

Pokrowsky[13] made use of a modified theory of Rayliegh in his investigations on the scattering of light by particles of water in a spray and to explain the experimental investigations of Dorno[14] on the scattering of light by atmospheric clouds.

Scope of the Work

But no work is available for the scattering of light by particles whose size is considerably greater than the wave-length of light. The greatest value of the radius of the drop for which Mie's theory has been worked out by Blumer[8] is $0 \cdot 8\ \mu$ for conducting spheres and $0 \cdot 3\ \mu$ for water drops.

It has been shown by various workers that the scattering of light by large dielectric spheres vary greatly from that by small spheres. Rayleigh's[1] formula as originally developed by him, being limited to small spheres, cannot fully account for the uneven distribution of light by large spheres. The asymmetry of scattering increases rapidly with the increase of the size of the sphere and the light scattered in the forward direction becomes very great as compared to that scattered in the backward direction.

In the present papers, the theoretical and experimental investigations have been extended on the basis of Mie's theory to much larger particles. The values of $\alpha = \frac{2\pi\rho}{\lambda}$ selected for calculations were 4, 5, 6, 7, 8, 9, 10, 15, 20 and 30, where ρ = radius of the particle and λ = wave-length of light. Thus the theoretical picture of the scattering of light in a medium as built up of particles of water whose radius varies from nearly $0 \cdot 4\ \mu$ to $3\ \mu$ has been obtained for the first time.

Theory of Light Scattering

This problem of scattering of light has been solved by Mie[3] by applying Maxwell's equations of light propagation. By integrating these equations for the field inside and outside the particle, Mie calculates the amplitudes of the waves of light radiated by the particle in various directions. The equations include a series of partial waves into which the total radiation of the particle is divided.

Mie then modified the above relations and obtained the following forms which give the intensity of scattered light, for a beam of unpolarised light incident on the particle. Mie separates the scattered light into two components, *viz.*, (i) the intensity I_1, whose electrical oscillations are perpendicular to the plane of sight, *i.e.*, polarised in the horizontal plane containing the observed scattered beam and the incident beam ; and (ii) the intensity I_2, whose electrical oscillations are in the plane of sight, *i.e.*, polarised in the vertical plane. I_1 and I_2 are given as follows :—

$$I_1 = \frac{\lambda^2}{4\pi^2\gamma^2}\left|\sum_{n=1}^{\infty}\{A_n\,\pi_n + P_n\,[\pi_n.\mu - \pi_n'\,(1-\mu^2)]\}\right|^2$$

$$I_2 = \frac{\lambda^2}{4\pi^2\gamma^2}\left|\sum_{n=1}^{\infty}\{A_n\,[\pi_n\,\mu - \pi_n'\,(1-\mu^2)] + P_n\,\pi_n\}\right|^2,$$

where $A_n = \frac{a_n}{n\,(n+1)}$ and $P_n = \frac{p_n}{n\,(n+1)}$, ...

n is the serial number of a partial wave ; $\mu = \cos\gamma$, $(\pi - \gamma)$ being the angle of the scattered ray with the direction of the incident ray ; a_n and p_n are complex functions depending on the wave-length of light λ, radius of the particle ρ and the refractive index m' of the material of the particle with respect to the surrounding medium. π_n and π_n' are the function and its derivative respectively of $\cos\gamma$. The $|\ |^2$ sign indicates that the square of the absolute value in the parenthesis is taken.

The scattered light is observed in the horizontal plane and hence I_1 is the intensity of light, which is plane polarised in the horizontal plane and I_2 is the intensity of light, which is plane polarised in the vertical plane. The sum $(I_1 + I_2)$ gives the full intensity of light and the difference $(I_1 - I_2)$ gives the surplus polarised light. If the difference is positive the light is polarised in the horizontal plane, and if it is negative the light is polarised in the vertical plane.

The values of A_n, P_n, π_n and π_n' were obtained from the Mie's formula, and were used in obtaining the results of I_1 and I_2 for the different values of α mentioned above. The functions A_n and P_n involve a number of Bessel function series depending on α and $\beta = m'\alpha$. Some of the values of the Bessel function series for integral values of α were taken from the British Association Reports, 1914, 1916 and 1922, while the series for all fractional and larger integral values of α and $\beta = m'\alpha$ were evaluated. A calculating machine and seven figure logarithm tables were used to obtain the values of the above functions. The factor $\frac{\lambda^2}{4\pi^2\gamma^2}$, which is a constant is omitted in the results of I_1 and I_2.

Results

The results of calculations are given in the following tables. The first column gives the angle of scattering, the angle being taken zero for the backward direction. The second and third columns give the values of I_1 and I_2 the values of the horizontally and vertically polarised light respectively. The last column gives P, the percentage of surplus polarised light. The sign + indicates that the light is polarised in the horizontal plane, which is the plane of observation ; while the sign — indicates that it is polarised in the vertical plane.

The results are plotted in Fig. 1 ($a - k$). Each curve is divided into two parts. The values of the intensity of scattered light for angles between 0° to 130° are plotted on a magnified scale ; while those beyond 130° are plotted on a smaller scale. Again, as the relative values of the intensities for higher values of a are very large, the results for $a = 15$, 20 and 30 are plotted on half the scale than the rest.

TABLE I

$a = 4$ $\beta = 5 \cdot 32$ $m' = 1 \cdot 33$

γ in degrees	I_1	I_2	$I_1 + I_2$	P
0	7·350	7·350	14·700	0
10	5·742	5·190	10·932	+ 5·06
20	4·197	2·728	6·925	+ 21·21
30	2·001	0·857	2·858	+ 34·02
40	0·749	0·560	1·309	+ 14·47
50	0·047	1·216	1·263	− 13·42
60	0·208	1·345	1·553	− 13·95
70	2·498	0·056	2·554	− 95·63
80	0·714	0·969	1·683	− 15·18
90	2·727	0·516	3·244	+ 68·17
100	0·968	0·100	1·067	+ 81·36
110	1·994	3·051	5·045	− 20·95
120	1·951	2·060	4·011	− 2·71
130	5·490	7·607	13·098	− 15·40
140	16·818	20·888	37·706	− 10·30
150	42·662	45·848	88·510	− 3·60
160	79·227	81·319	160·546	− 1·30
170	114·441	114·849	229·290	− 0·08
180	125·240	125·240	250·480	0

TABLE II

$\alpha = 5 \quad \beta = 6{\cdot}65 \quad m' = 1{\cdot}33$

γ in degrees	I_1	I_2	$I_1 + I_2$	P
0	0·0662	0·662	0·1324	0
10	0·352	0·345	0·697	+ 1·0
20	0·678	0·578	1·256	+ 7·9
30	1·240	0·888	2·128	+ 16·5
40	1·820	1·723	3·543	+ 2·7
50	1·904	0·700	2·604	+ 7·8
60	0·840	0·178	1·018	+ 65·0
70	0·271	0·052	0·323	+ 67·8
80	0·040	0·141	0·181	− 55·8
90	0·396	0·076	0·472	+ 66·7
100	0·192	0·235	0·427	− 10·0
110	0·243	0·552	0·895	− 34·5
120	1·183	0·652	1·835	+ 28·9
130	3·599	0·306	4·905	+ 67·1
140	0·404	0·540	0·944	− 14·4
150	9·260	6·190	15·450	+ 19·8
160	62·160	56·090	118·250	+ 5·1
170	141·620	133·470	275·090	+ 2·9
180	197·220	197·220	394·440	0

TABLE III

$\alpha = 6 \quad \beta = 8 \quad m' = 4/3$

γ in degrees	I_1	I_2	$I_1 + I_2$	P
10	2·34	3·18	5·52	− 15·1
30	6·65	3·83	10·48	+ 26·9
50	0·34	0·06	0·40	+ 71·7
70	4·59	1·71	6·30	+ 45·7
90	3·51	3·42	6·93	+ 1·2
100	7·85	4·25	12·10	+ 29·7
110	2·27	6·05	8·32	− 45·4
120	1·61	7·40	9·01	− 64·4
130	30·46	25·30	55·76	+ 9·2
140	24·95	31·50	56·45	− 11·6
150	42·18	71·46	113·64	− 25·8
160	332·36	353·95	686·31	− 3·1
170	912·12	904·58	1816·70	+ 0·4
180	1237·15	1237·15	2474·39	0

TABLE IV

$\alpha = 7 \quad \beta = 9{\cdot}31 \quad m' = 1{\cdot}33$

γ in degrees	I_1	I_2	$I_1 + I_2$	P
0	6·495	6·495	12·990	0
10	1·551	5·243	6·794	− 54·31
20	7·854	6·806	14·660	+ 7·50
30	9·820	4·576	14·396	+ 36·42
40	1·082	1·524	2·606	− 16·97
50	6·862	2·309	9·171	+ 49·65
60	5·564	2·626	8·190	+ 35·82
70	0·165	4·269	4·434	− 92·55
80	7·060	3·883	10·943	+ 29·04
90	3·902	3·205	7·107	+ 9·80
100	2·394	7·954	10·348	− 29·04
110	15·465	12·113	27·578	+ 12·13
120	16·262	18·107	34·369	− 5·36
130	20·320	29·291	49·611	− 18·09
140	73·795	72·709	146·504	+ 0·74
150	47·067	73·762	120·829	− 22·18
160	298·437	337·838	636·275	− 6·19
170	1355·033	1366·879	2721·912	− 0·43
180	496·700	496·700	993·400	0

TABLE V

$\alpha = 8$ $\beta = 10{\cdot}64$ $m' = 1{\cdot}33$

γ in degrees	I_1	I_2	$I_1 + I_2$	P
0	38·20	38·20	76·40	0
10	4·21	7·05	11·26	− 25·2
20	18·12	4·65	22·77	+ 59·1
30	12·16	4·47	16·63	+ 46·2
40	3·73	5·37	9·10	− 18·0
50	2·68	26·39	29·07	− 81·5
60	10·46	15·09	25·55	− 18·1
70	14·89	1·65	17·54	+ 75·4
80	1·73	4·34	6·07	− 43·0
90	10·25	4·90	15·15	+ 35·3
100	2·77	4·19	6·96	− 20·4
110	1·68	29·74	31·42	− 89·3
120	49·46	70·16	119·62	− 17·3
130	33·23	24·14	57·37	+ 15·8
140	42·64	90·33	132·97	− 36·8
150	158·92	131·53	290·45	+ 9·4
160	330·52	387·10	717·62	− 8·0
170	1415·30	1583·30	2998·60	− 5·6
180	2922·05	2922·05	5844·10	0

TABLE VI

$\alpha = 9 \quad \beta = 12 \quad m' = 4/3$

γ in degrees	I_1	I_2	$I_1 + I_2$	P
10	5·07	8·64	13·71	− 16·1
30	4·85	1·41	6·27	+ 54·8
50	1·92	7·71	9·43	− 63·5
70	1·92	5·15	7·06	− 45·8
90	4·66	6·90	11·56	− 19·4
100	4·54	4·94	19·48	− 53·4
110	16·30	15·13	31·43	+ 3·7
120	11·96	36·22	48·18	− 50·3
130	66·29	60·13	126·42	+ 4·9
140	32·55	70·43	102·98	− 36·7
150	275·01	262·30	537·31	+ 2·5
160	106·51	128·55	235·06	− 9·4
170	1256·05	1402·55	2658·61	− 4·5
180	3466·47	3466·48	6932·95	0

TABLE VII

$\alpha = 10 \quad \beta = 13 \cdot 30 \quad m' = 1 \cdot 33$

γ in degrees	I_1	I_2	$I_1 + I_2$	P
0	19·94	19·94	39·98	0
10	28·23	5·66	33·89	+ 66·6
20	78·15	20·31	98·46	+ 58·7
30	3·83	62·76	66·59	− 88·5
40	60·80	29·10	89·90	+ 35·3
50	2·52	2·95	5·47	− 7·8
60	35·08	10·06	45·14	+ 45·3
70	6·78	10·69	17·57	− 22·3
80	1·06	35·95	37·01	− 94·3
90	5·29	4·45	9·74	+ 8·6
100	11·50	52·00	63·50	− 63·9
110	35·64	10·24	45·88	+ 55·3
120	21·16	51·08	72·24	− 41·4
130	73·68	50·38	124·06	+ 18·8
140	58·49	106·07	164·56	− 28·9
150	174·50	154·04	328·53	+ 6·2
160	197·93	276·48	474·41	− 16·6
170	622·13	649·84	1271·97	− 2·2
180	2767·31	2767·31	5534·62	0

TABLE VIII

$a = 12 \quad \beta = 16 \quad \gamma' = 4/3$

γ in degrees	I_1	I_2	$I_1 + I_2$	P
0	33·97	33·97	67·94	0
10	26·40	32·27	58·67	− 5·9
20	21·71	32·37	54·08	− 11·7
30	34·16	27·59	61·75	+ 6·6
45	24·60	34·76	59·36	− 10·2
60	4·78	2·89	7·67	+ 1·9
70	5·48	3·69	9·17	+ 1·8
80	1·01	8·77	9·78	− 7·8
90	2·09	1·99	4·08	+ 0·1
100	13·15	14·64	27·79	− 1·5
110	23·61	25·00	48·61	− 1·4
120	20·12	21·02	41·14	− 0·9
135	51·89	50·50	102·39	+ 1·4
150	165·14	170·52	335·66	− 5·4
160	216·14	228·69	444·83	− 12·5
170	601·61	602·71	1204·32	− 1·1
180	845·25	845·25	1690·50	0

(These results are taken from Rayleigh and Ray's calculation.)

TABLE IX

$a = 15 \quad \beta = 20 \quad m' = 4/3$

γ in degrees	I_1	I_2	$I_1 + I_2$	P
10	58·42	215·07	273·49	− 57·2
20	36·24	12·63	48·88	+ 48·3
30	23·04	3·22	26·27	+ 75·4
40	0·22	54·71	54·94	− 99·2
50	5·59	12·05	17·64	− 36·6
60	13·70	17·10	30·79	− 11·0
70	9·25	16·03	25·28	− 26·8
80	9·72	24·05	33·77	− 42·4
100	8·08	47·00	55·08	− 70·6
110	4·29	114·39	118·68	− 92·8
120	35·22	52·87	88·09	− 20·0
130	115·82	93·31	209·14	+ 10·8
140	199·21	254·94	454·15	− 12·3
150	137·24	184·17	321·41	− 14·6
160	299·93	157·40	457·33	+ 31·2
170	4482·59	3589·95	8072·34	+ 11·0
180	22781·35	22781·35	45562·70	0

TABLE X

$a = 20$ $\beta = 26{\cdot}66$ $m' = 1{\cdot}333$

γ in degrees	I_1	I_2	$I_1 + I_2$	P
10	22·40	425·44	447·84	− 90·0
20	97·18	120·24	217·42	− 10·6
30	65·08	3·92	69·00	+ 88·6
40	38·53	59·34	96·97	− 20·4
50	48·68	67·58	116·27	− 16·2
60	24·06	12·07	36·14	+ 33·2
70	2·94	5·13	8·07	− 27·1
80	4·41	43·36	47·77	− 81·5
90	4·23	55·63	59·85	− 85·8
100	2·33	30·52	32·85	− 85·8
110	1·28	38·24	45·52	− 68·0
120	15·92	118·14	134·06	− 76·2
130	22·10	234·82	257·02	− 82·7
140	43·03	272·41	315·44	− 72·7
150	108·95	344·11	453·06	− 51·9
160	641·96	728·12	1370·08	− 6·3
170	890·00	1531·99	2421·99	− 26·5
180	45871·00	45871·00	91742·00	0

TABLE XI

$\alpha = 30 \quad \beta = 40 \quad m' = 4/3$

γ in degrees	I_1	I_2	$I_1 + I_2$	P
10	282·42	74·18	356·60	+ 58·4
30	140·67	55·16	195·82	+ 43·7
50	33·27	45·24	78·51	− 15·2
60	29·70	17·79	47·49	+ 25·1
80	4·56	9·94	14·50	− 37·1
90	30·27	18·11	48·39	+ 25·1
100	6·39	62·23	68·61	− 81·4
120	17·73	178·08	195·81	− 81·9
130	297·68	368·50	666·18	− 10·6
150	1025·98	1042·40	2068·39	− 0·8
170	9957·64	9163·53	19121·17	+ 7·1
180	195719·0	195719·0	391438·00	0

Discussion of Results

It can be seen clearly that fluctuations in the intensity distribution of light are more pronounced in the backward direction for all values of α in the present cases. It has been shown by Blumer[3] that for particles sizes for which α is less than 3, these fluctuations in the intensity of scattered light in the backward direction are considerably smaller.

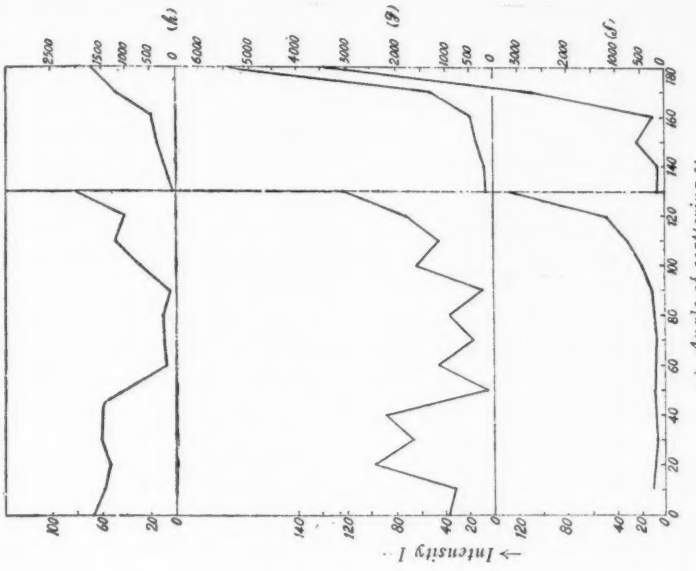


FIG. 1. *f, g, h*

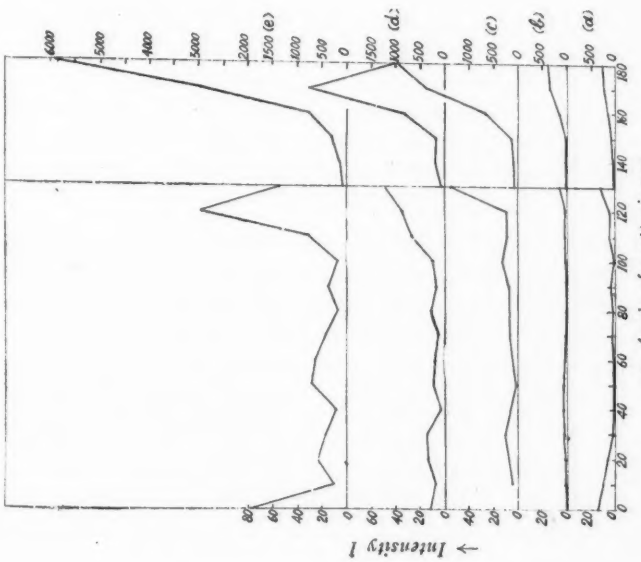
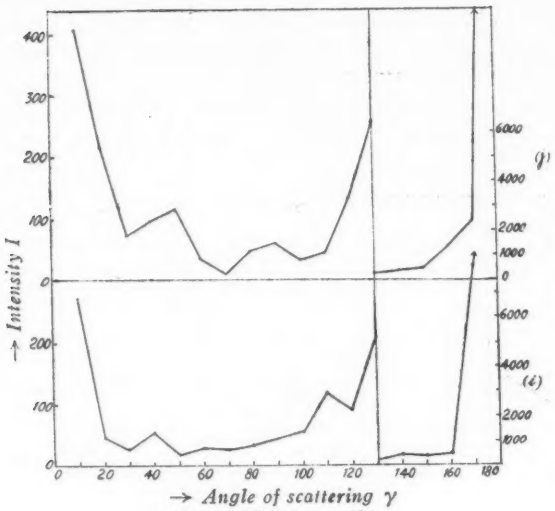
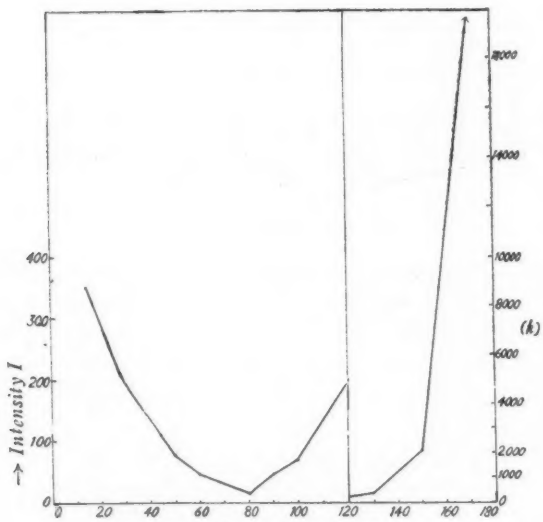


FIG. 1. *a, b, c, d, e*



(i) $\alpha = 15$, (j) $\alpha = 20$,

FIG. 1. *i, j*



$\alpha = 30$

FIG. 1. *k*

From Fig. 1 (*a*-*k*) it can be seen that as the value of α becomes larger than 4, the fluctuations in the intensity of scattered light in the backward direction become more pronounced. For $\alpha = 4$ and 5 the fluctuations are comparatively smaller in magnitude, but they become more and more pronounced as α approaches the value 8. For $\alpha = 8$, the symmetry of scattering is very large. For $\alpha = 9$, the intensity fluctuations become again less pronounced, but for $\alpha = 10$ the asymmetry of light-scattering is remarkable and shows a very large fluctuation for different angles. For $\alpha = 12$ and 15 the fluctuations are less pronounced and again for $\alpha = 20$, the fluctuations become more remarkable. The curve for $\alpha = 30$ shows only a gradual change of the intensity of scattered light and for larger values of α, it is possible that the fluctuations may gradually disappear and that the nature of the distribution of the scattered light may approximate to that indicated by Shoulejkin[15] from his calculations on the basis of the sacttering by reflection and refraction only.

In the forward direction, *i.e.*, for angles larger than 90°, there are not many fluctuations in the intensity of light distribution for different values of α. Again there is a gradual rise in the intensity of scattered light for all angles greater than about 120°, except for the case of $\alpha = 7$, where it is found that the intensity falls down to a considerably smaller value at $\gamma = 180°$ than that for $\gamma = 170°$. For values of α smaller than 3, the scattering in the forward direction has a large number of maxima and minima which are nearly completely absent for all the present cases. The comparative distributions of intensities for different values of α in the forward direction indicate that the values become large as α increases. The differences in the intensities for angles less than 90° are not very large for different values of α. It is only in the neighbourhood of 180° that the values of intensity increase very rapidly with the increase in the value of α, *i.e.*, with the increase of the size of the drop.

The other important fact that one observes is that the total amount of light scattering in the forward direction is considerably larger than that in the backward direction for all values of α. For smaller particles the reverse is the case. This leads us to conclude that as the sphere becomes larger the scattering in the forward direcion becomes more and more pronounced. For very large dielectric spheres the scattering may approximate to the distribution as explained by Shoulejkin[15].

For all the sizes of the particles the polarisation for different angles shows maxima and minima. The preponderance of I_2 component over I_1, has been denoted by negative polarisation. In the backward direction the polarisation

is found to be both positive and negative, but in the forward direction, it remains essentially negative except for $a = 5$. The maximum polarisation is found to be in the backward direction except for $a = 30$. The polarisation for $a = 12$ is found to be a minimum as compared to that all other values of a. The values of the scattered intensities of light for this case ($a = 12$) have been taken from the results of Rayleigh[1] and Ray.[9]*

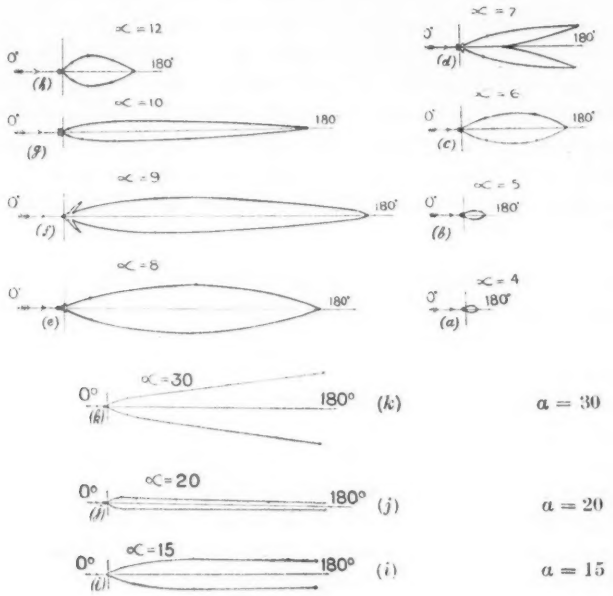


FIG. 2 (a—k)

(Curves i, j, k, are drawn on 1/2 scale than others)

The intensity distribution is also indicated by means of polar diagrams in Fig. 2 (a—k). They clearly indicate how the nature of the intensity distribution changes with the increase of the size of the sphere. The curves become longer and narrower in the forward direction for larger values of a. It is also seen that the curves for $a = 10$ and $a = 12$ indicate less scattering in the forward direction as compared to other values of a.

* The evaluation of the intensity of scattered light for $a = 12$ by Mie's formula has recently been completed and it is found that there is a close agreement between the two values upto 130°; for larger angles the values are larger than those of Rayleigh.

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SCATTERING OF LIGHT BY LARGE WATER DROPS—PART II

By G. R. Paranjpe, Y. G. Naik and P. B. Vaidya
(From the Department of Physics, Royal Institute of Science, Bombay)

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In Part I of this paper we gave detailed calculations of the intensity and polarisation of light-scattering by large water drops particularly with a view to study the angular distribution of intensity and its dependence on the particle sizes. The present part concerns itself with an experimental study of the subject.

As has been pointed out earlier that the available experimental data on the scattering of light are very meagre, the problem of scattering of light by dielectric spheres of sizes comparable to, or greater than, the wave-length of light has not been worked out before in detail.

Previous Work

The experimental works of Keen and Porter[16], Ray[9] and others are restricted mainly to small colloidal particles, and the scattering is measured either along the direction of light or in a transverse direction. Benedict and Senftleben[17] were the first to study systematically the scattering of light by small particles in different directions.

Pokrowsky[13] worked on water drops formed by sudden condensation of water vapour. The average size of drops in his experiments was considerably smaller than the wave-length of light, the greatest value of $\alpha = \frac{2\pi\rho}{\lambda}$ being 0·67. Konig-Marten's sector-photometer was employed to determine the intensity of the polarisation of the scattered light and the intensity of one of the components. The results of his observations for intensity and polarisation agree well with those calculated according to the theory. He also applied an approximation of Rayleigh's theory in the explanation of his experimental work on the scattering of light by water drops in different directions within 5 degrees from the forward direction.

Webb[18] has investigated recently the scattering of light by large drops of water and alcohol-water mixture. The drops were illuminated by a parallel beam of light from a carbon arc and the intensity of the scattered light was recorded on a photographic plate. His observations, however, are likely to

have been affected by the inconstancy of the arc, the growth of the drops in the process of condensation, and uncertainty in the number of scattering drops.

Borne[19] used copper oxide photo-cells, one to measure the intensity of the scattered light by cigarette and ammonium chloride smokes illuminated by a 5000 watt lamp, and another to measure the intensity of the source. The particle size was, however, considerably smaller than the wave-length of light.

Work of this type has usually to contend with two difficulties. One of them refers to the production of fairly large, stationary and uniform dielectric spheres. The other is the estimation of their number and dimensions. The theoretical working out of the problem as mentioned in the first part is also very laborious and becomes unwieldy for large spheres. It is on account of these difficulties perhaps that this problem has not been pursued in much detail.

Production of steady clouds, the determination of the size of the drops and the transmission of light have been subjects of study for a long time by means of the apparatus used in the present work. It has been possible to overcome the difficulties mentioned before, and a fairly stable cloud of uniform density and of any desired particle size of radius, between 1 to 12 μ can be now produced. The instantaneous determination of the size of the drops by the corona ring method and the stability of cloud have been of special advantage in the present work. It must be emphasised that the uniformity of the size of water-drops in the cloud is of very great and fundamental importance in the work on scattering. A slight change in the size of the drops changes the general character of the scattering very much. The details of these experiments have been given in a number of papers[20].

Production of a Cloud of Water Drops

The clouds on which the present investigations were carried out were formed inside a flask of about 12 litres capacity by adiabatic expansion. This expansion was effected by connecting this flask suddenly to a large tank in which a suitable low pressure was created by means of a vaccum pump. This tank was connected with the flask through a tube of wide bore, whose cross-section was about 1 sq. inch. The instantaneous connection between the flask and the tank was made by means of a cock of a larger cross-section. A small quantity of water or liquid to be experimented upon was kept inside the flask.

When a sudden expansion of any desired magnitude is made, a fixed quantity of liquid is available for condensation and this liquid distributes

itself on the number of nuclei available in the flask. Thus, by controlling the entry of dust nuclei into the flask and the expansion ratio, a cloud of any desired size of drops can be produced. In order that the vapour may not condense on the sides of the flask and that the air inside the flask may remain saturated, it was vigorously shaken every time so as to wet all the inside surface.

Care was taken during the experiments to see that the cloud produced was of uniform density and that the size of the drops for any particular set of measurements was kept the same. This was achieved by producing a large number of smoke particles (size less than about 50 $\mu\mu$) from a particular brand of incense stick in a large cupboard of about 4000 litres capacity. The smoke was allowed to be diffused and co-agulated in the initial stages, after being thoroughly mixed by means of a fan, for a period of at least an hour or more before the actual measurements were made. This ensured the density of smoke particles in the cupboard to be the same. It was found that the decrease in the number of smoke particles in the beginning is very rapid and that it becomes extremely slow after about an hour. As any set of measurements takes not more than an hour, one can neglect any small variation in the number of smoke particles. A measured quantity of this smoke-bearing air from the cupboard was allowed to enter the expansion flask every time.

With a little experience it was possible to control the entry of smoke-bearing air from the cupboard into the flask as also the expansion ratio, so that a cloud of uniform density and of desired size of drops could be produced.

The size of the drops in the cloud was determined or checked by the corona rings seen by looking at a distant source of light through it. The angular aperture of the corona ring in monochromatic light serves as a method of determining instantaneously the size of the drops. The wave-length of light, the size of the drops and the angular aperture of the corona are related with each other as follows :—

$$\text{Sin } \theta = (n + 0{\cdot}22)\frac{\lambda}{2\rho},$$

where 2θ = angle subtended by the diameter of a corona ring minimum at the eye of the observer.

n = the order of the ring.

λ = mean wave-length of the light forming the corona.

ρ = average radius of the drops.

A well-defined circular corona ring attains its final size in less than a second and remains stationary till the cloud settles down. The well-defined

circular shape of the corona suggests that the drops are nearly of the same size. The final steady size of the corona indicates that the drops do not evaporate appreciably during the course of the experiment.

In some experiments, when the drops were smaller than 2 μ in radius, the corona method was used only as a check for the size of the drops, and not directly to determine it. It is found in actual practice that the size of the corona is well-defined for all drops of radii larger than 2 μ. Wilson[21] and Mecke[7] have also shown that the corona theory is applicable only to drops whose radii are greater than 2 μ. Even for drops of 2 μ radii, the corona is very large and diffuse and hence the size was checked by the Stokes' law as corrected by Bromwich[22] and Cunningham[23]. A check was also obtained by a subsequent experiment in which only a known fraction of the air from the cupboard was introduced and a well-defined corona was observed in the cloud. This experiment indicated how many nuclei were there in the large cupboard. Knowing this and the total volume of nuclei-bearing air that was introduced into the flask for actual experiment, the value of the size of the drops, when less than 2 μ in radii, was determined. It was found that the two values agreed well within an error of about 5%. The contribution by the nuclei within the drops to the scattered light is quite negligible. It was therefore, not necessary to make any correction in the intensity measurements on this account.

Intensity Measurement

In order to measure the intensity of light scattered by a beam of parallel rays in any given direction a source of light S_2 was taken. S_1 is another lamp, kept at a great distance and is used to obtain the corona rings in the cloud. A monochromator M is used to facilitate the measuring of the intensity of scattered light of a particular wave-length (Fig. 1).

In order that the intensity of the scattered light may be as large as possible, the source of light S_2 was kept within the wooden chamber in which the experimental flask was kept and the monochromator was also pushed as near to the flask as possible. In order to change and measure the direction of scattered light entering the monochromator a spectrometor table was used. The flask F in which the cloud was produced was placed at the centre of this table and along the axis of the collimator of the monochromator. The source of light S_2 along with the lens L_2 and diaphram DD' was mounted on an arm of the spectrometer table. A heavy weight is attached to the other side of the arm as a counterpoise. The arm, being attached to a vernier scale moving on the main circular scale of the spectrometer table, can be rotated and fixed to any desired angle.

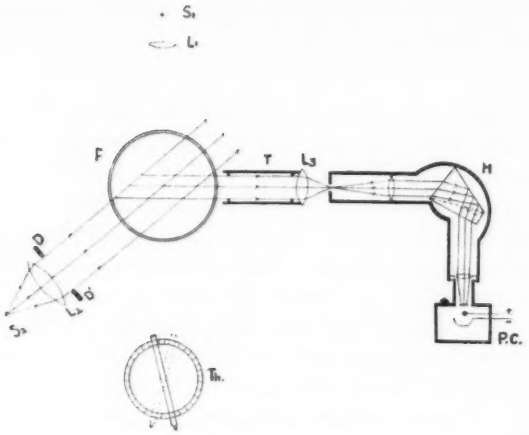

FIG. 1

S_1 & S_2—Sources of light; L_1 & L_2—Collimating lenses; DD'—Diaphram; F—Condensation flask; T—Collimating tube; L_3—Lens; M—Monochromator; $P.C.$—Photo-cell; Th—Theodolite.

The actual intensity of light is measured by means of a photo-cell P.C. attached to the monochromator. The diagrammatic sketch of the connections of the photo-cell is shown in Fig. 2.

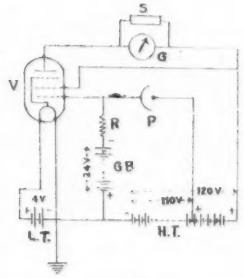

FIG. 2

The temperature of the air surrounding the cloud chamber was observed every now and then. As the cloud chamber is placed in a large enclosure there was very small variation of temperature in its neighbourhood. It was observed that if the lamp S_2 was kept on for a long time there was a small rise in the temperature of the enclosure and hence care was taken to switch on this lamp only for a short time for the measurement of the scattered intensity.

The coiled filaments of lamp S_2 were in one plane in the form of a square and hence gave a beam of uniform intensity. This light was made parallel by a lens mounted on the same arm of the spectrometer table as the source. The lens had a large aperture so that a rectangular beam of light was passing through the cloud. One more diaphram was placed between the lens and the cloud chamber. The lamp was so placed that the boundaries of this beam were in the horizontal and vertical planes. In order that the intensity of light of this lamp may remain constant, it was connected to a separate storage battery.

The scattered beam was allowed to pass through a tube with a slightly smaller cross-section and was then focussed by means of a lens on the slit of the monochromator. It was ascertained that no extra light fell on the slit. The aperture of the tube receiving the scattered light was kept small to facilitate the estimation of the correction for the volume and number of actual scattering particles, when the incident beam is rotated through different angles.

The incident direction of light was every time ascertained before beginning any set of observations by first adjusting the position of the lamp in such a way that the photo-cell gave a maximum deflection for direct light incident on the slit of the monochromator. As a further check on the measurements it was ascertained that with a given cloud, equal rotations of the lamp S_2 on either side of this position, gave the same current through the photo-cell. This adjustment ensured the correctness of the observations for different angles of scattering.

The photo-cell was found to work very satisfactorily. Initially there used to be a very large fluctuation in the dark current, but later on by earthing the box containing the cell as also the one containing the amplifying circuit, the fluctuation disappeared. The readings obtained after this improvement were consistent and could be reproduced. The photo-cell was most sensitive in the red region and hence the monochromator was adjusted to select a wave-length in this region.

Volume Correction

As the incident beam of light illuminates only a small portion of the cloud in the flask, the effective volume of cloud which scatters light varies with the angle of scattering. From Fig. 3 (*a*, *b*) it is clear that the volume of cloud responsible for the scattering of light in a given direction depends on the angle at which the scattered light is received in the monochromator. Evidently the volume responsible for scattering is more for angles nearer to 0° or 180°. For angles near about 90°, the volume of cloud scattering the

light is a minimum. The volume of intersection of the incident beam and the scattered beam will be a function of the angle γ and it can be expressed by $\frac{V_0}{\sin \gamma}$, where V_0 is the volume of intersection at 90°. (This will hold good only for $\gamma > \frac{2D - b}{a}$, where $2D$ = breadth of the incident beam ; $2b$ = diameter of the scattered beam ; a = radius of the flask.)

This determination is necessary because in the present case the scattering of light is not due to an isolated sphere, but due to a large number of particles distributed uniformly in the cloud.

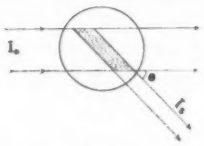

FIG. 3, *a*

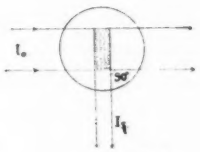

FIG. 3, *b*

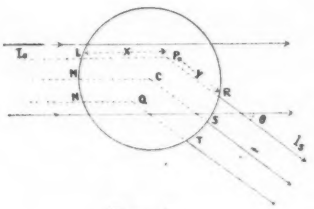

FIG. 4

If we assume the approximate formula of light-absorption in a cloud of drops as given by Jöbst[24], Debye[5], Anderson[25], and modified by Houghton[26] we find that the intensity of light I′ reaching a sphere P well within the flask (Fig. 4) will be given by

$$I' = I_0 \times e^{-kx}$$

where I_0 = intensity of incident light on P ;

k = constant ;

and X = distance of the sphere P from the boundary of the flask where the light enters the cloud.

This light will be scattered by that drop in all directions and the intensity of light coming out in any given direction γ will be further absorbed for a distance Y within the flask. The intensity of scattered light I″ by P in a direction γ will therefore be given by

$$I'' = I_0 \times e^{-kx} \times F(\rho, \lambda, m', \gamma),$$

where $F(\rho, \lambda, m', \gamma)$ is a scattering function depending on the radius of the drop, the wave-length, the refractive index and the angle of scattering, γ.

This scattered light will suffer further absorption due to a path Y within the flask and hence I_s the actual intensity of scattered light coming out along γ will be given by

$$\begin{aligned} I_s &= I'' \times e^{-kv} \\ &= I_0 \times e^{-kx} \times e^{-kv} \times F(\rho, \lambda, m', \gamma) \\ &= I_0 \times e^{-k(x+v)} \times F(\rho, \lambda, m', \gamma). \end{aligned}$$

If there are N particles scattering the light, the total intensity coming out along a direction γ will be

$$I_s = I_0 \times N \times e^{-k(x+v)} \times F(\rho, \lambda, m', \gamma).$$

If we try to find out the average length of the path (X + Y) within the flask of the incident and the scattered light by various particles, we shall obtain (X + Y) = 2*a* where *a* is the radius of the flask.

This becomes clear from Fig. 4 in which we find that for a particle P the length of path of light is (LP + PR) for one at C the path is (MC + CS) = 2*a* and for Q it is (NQ + QT). Again (LP + PR) > 2*a* > (NQ + QT), and hence the average value of (X + Y) can be approximately taken equal to 2*a*.

The number of scattering particles N will be given by $N = nV$,

where n = number of drops per c.c.

and V = volume of the cloud scattering the light.

If V_0 = volume of intersection of the incident and the scattered beams when they are at right angles to each other (*i.e.*, when $\gamma = 90°$),

$$V = \frac{V_0}{\sin \gamma}$$

$$\therefore N = \frac{n V_0}{\sin \lambda}$$

Thus the final formula giving the intensity of scattered light in the present experimental arrangement is

$$I_s = I_0 \times \frac{n V_0}{\sin \gamma} \times e^{-2ak} \times F(\rho, \lambda, m', \gamma)$$

by taking $nV_0e^{-2ak} = C$ = a constant we get,

$$I_s = I_0 \times C \times F(\rho, \lambda, m', \gamma) \times \frac{1}{\sin \gamma}$$

$$\therefore \quad I_s \times \sin \gamma = I_0 \times C \times F(\rho, \lambda, m', \gamma).$$

$$= I.$$

Thus all observed values of I_s will have to be multiplied by sin γ in order to correlate them with the actual values of scattering I obtained from the scattering function F $(\rho, \lambda, m', \gamma)$.

Here it must be noted that the number of drops per c.c. is of the order of 2000 to 6000, and they little influence the final result on account of multiple scattering. Trincks[27] has pointed out in his recent paper that serious changes are required in Mie's result when two particles are very near. These changes become negligible when the separation of drops is greater than two or three particle diameter. The maximum average distance between two drops in the present investigations taking n to be equal to 8000, comes out to be 0·05 cm. The maximum diameter of the drops is 8 μ (·0008 cm.). Thus the ratio of the average distance to the maximum diameter turns out to be 62·5°. Thus it is clear that multiple-scattering does not affect the final result. As a further check, experiments were performed by collimating the incident light with apertures of different sizes in any fixed direction. Tests carried out at three different angles indicated that keeping all the factors constant and varying only the number of scattering particles by changing the aperture of the incident beam, the intensity of the scattered light was proportional to the number of particles.

Experimental Results

To verify the theoretical results, experiments were performed for three particle sizes, *viz.*, $\alpha = 10$, 20, and 30. The results are expressed as factors proportional to the ratio of the scattered light to the incident light, and are given below after applying the necessary volume-corrections for different angles. The wave-length of light was taken to be 6800 A.U. for all the measurements. γ gives the angle of scattering and I is the final value of the scattered light corected for volume.

Results

TABLE I			TABLE II			TABLE III		
γ in degrees	I Theoretical $a=10$	I Experimental $a=10\cdot12$ $\rho=1\cdot096\mu$	γ in degrees	I Theoretical $a=20$	I Experimental $a=20\cdot22$ $\rho=2\cdot19\mu$	γ in degrees	I Theoretical $a=30$	I Experimental $a=30\cdot30$ $\rho=3\cdot28\mu$
25	80·0	103	40	97·0	92	40	130·0	125
40	89·9	67	50	116·3	75	50	78·5	95
60	45·1	30	60	36·1	45	60	47·5	60
75	25·0	27	70	8·1	36	70	40·0	52
90	9·7	28	80	47·8	30	80	14·5	35
105	55·0	36	90	59·9	45	90	48·4	38
120	72·2	80	100	32·9	50	110	130·0	125
135	140·0	125	110	45·5	76	120	195·8	212
150	328·5	286	120	134·0	130	130	666·2	690
160	475·0	492	130	257·0	216	140	1367·0	1275
170	1274·0	829	140	315·4	312	150	2068·0	2300
			150	453·1	500	160	10540·0	4810*
			160	1370·1	1140			

Discussion of Results

The experimental results for $a = 10\cdot12$ are shown by a graph in Fig. 5 along with the theoretical curve for $a = 10$. It is seen from the nature of the curve that the maxima and minima are not observed at all in the experimental curve. The average lay-out of the curve in the backward direction is however along a mean path of the theoretical curve. The maxima and minima cannot be expected to be observed experimentally for reasons described later. In the forward direction the curve is in very good agreement with the theoretical curve, except for angle 170°. This angle lies within the limit $\gamma = \frac{2D - b}{a}$ and hence the correction $\frac{V_0}{\sin \gamma}$ does not hold good for this value. For all small angles smaller than 12·5°, the same correction $\frac{V_0}{\sin 12\cdot5^\circ}$ holds good, in the present case. The discrepancy in the result therefore disappears as the value of the intensity as corrected above becomes 1033 instead of 829.

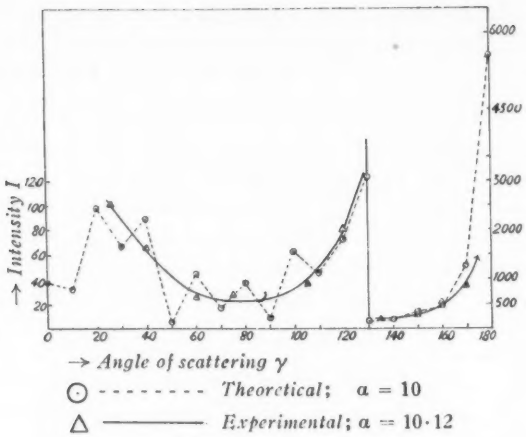

FIG. 5

The experimental curves for $\alpha = 20$ and 30 plotted in Figs. 6 and 7 respectively, lend further proof to the theory of Mie for larger drops. In the backward direction the intensity from 40° to 70° decreases rapidly, from 70° to 110° the decrease is small and from 120° onwards the increase is very rapid. The experimental curves appear to agree very well with the theoretical ones, in both the forward and the backward directions. It is found

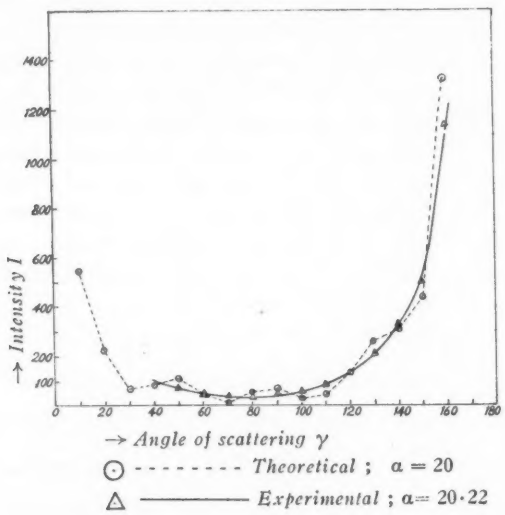

FIG. 6

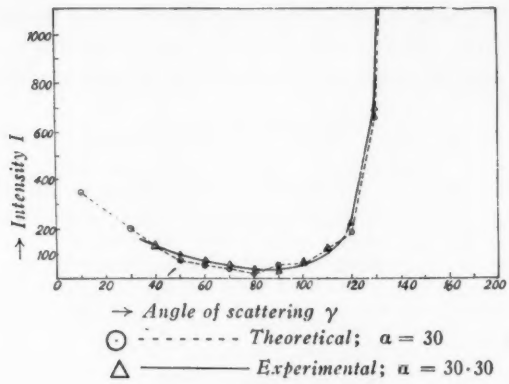

FIG. 7

that the general lay-out of the curves coincides with a mean hypothetical curve running through the theoretical one. The individual readings of the intensities differ from the theoretical ones to an extent of ± 17 per cent. These discrepancies can be attributed to various factors mentioned below. (The result marked with an asterisk in Table III deviates considerably from the theoretical value.)

The readings of intensities at least for three different angles were taken consecutively in one cloud formation. The adjustment of the angles had therefore to be done within a short time and hence could be adjusted correct to about 20 minutes. This gave rise to a maximum error of about 7 per cent. The collimation of light cannot be said to be perfect and hence some error due to the light being slightly diverging or converging is always likely to occur. Again the size of the drops may not be absolutely identical for all individual drops. The actual values of α in the experiments do not come out to be exactly in round numbers 10, 20 and 30 for which the theoretical curves have been obtained.

The above factors are also responsible for the fact that there were no maxima and minima observed in the experimental results. The general lay-out of all the curves however appear to verify Mie's theory quite well.

It can be observed from the curves that the quantitative agreement between the theoretical and experimental results is much closer in the forward direction than in the backward direction. As the intensity falls down considerably in the backward direction the errors in the intensity measurements are likely to be more than in the forward direction.

The experiments bring out clearly that for the study of scattering, or transmisson, of light it is essential that the size of the spheres in any

scattering medium must all be the same, and that the particles should not be too dense to give rise to multiple scattering. The theory of Mie is thus applicable not only to small particles but also to particles of any size as postulated by him.

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PIGMENTS OF COTTON FLOWERS

Part VIII. Constitution of Herbacitrin and Quercimeritrin

By P. Suryaprakasa Rao and T. R. Seshadri

(From the Department of Chemistry, Andhra University, Waltair)

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A new flavonol glucoside was recently isolated by Neelakantam and Seshadri from the Uppam (*Gossypium herbaceum*) cotton flowers and was named Herbacitrin.[1] It was shown to occur in the Karunganni (*G. indicum*) flowers also.[2] The glucoside on hydrolysis with acids yielded glucose and an aglucone called Herbacetin (formula I, R = H) whose constitution was arrived at by the above authors[3] from a study of its reactions and decomposition products and confirmed by Goldsworthy and Robinson[4] by synthesis.

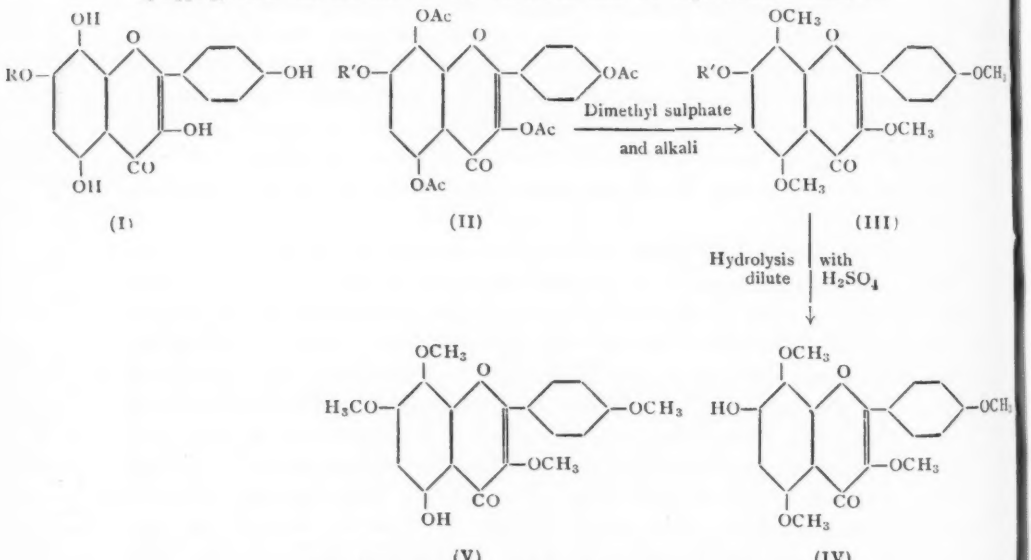
The new glucoside closely resembles Gossypitrin and also occurs along with it. When oxidised in alkaline solution, it yields *p*-hydroxybenzoic acid and hence the hydroxyl group in position 4 should be free. It gives a deep red precipitate with lead acetate and is hydrolysed with difficulty by acids, indicating thereby that it is not a 3-glucoside. The possibility of the 5- or the 8-hydroxyl group being involved in glucoside formation does not exist as the substance is readily oxidised to give the gossypetone reaction. From these considerations and also from the fact that all known glycosides of anthoxanthins are either the 3- or the 7-glycosides, Herbacitrin was tentatively represented by Neelakantam and Seshadri as the 7-glucoside of Herbacetin.[3]

For purposes of definitely orienting the position of the glucose residue, the use of diazomethane as a methylating agent is precluded since it does not methylate even Herbacetin completely,[5] the hydroxyl group in position 5 remaining unaffected. Our object has, however, been achieved by methylating Herbacitrin through its acetyl derivative, hydrolysing the methylated glucoside and identifying the partially methylated Herbacetin obtained thereby. This method of methylation through the acetyl derivatives has been recently used by us very successfully in the case of Gossypitrin.[6] Herbacitrin octa-acetate in acetone solution is treated with dimethyl sulphate and alkali alternately. The acetyl groups are removed and all the free phenolic hydroxyl groups get methylated. Hydrolysis of the product with

dilute sulphuric acid gives rise to an O-tetramethyl-herbacetin. There are two tetramethyl ethers of Herbacetin described in the literature :—(1) 3 : 7 : 8 : 4′-tetramethyl ether (V) recently prepared by us by the methylation of Herbacetin with diazomethane[5]; (2) 3 : 5 : 8 : 4′-tetramethyl ether (IV) obtained by Goldsworthy and Robinson (*loc. cit.*), in the course of the synthesis of Herbacetin. These are very easily distinguished from each other from their reactions with sodium hydroxide and ferric chloride. The product resulting from the hydrolysis of the methylated glucoside agrees with (IV) very closely as shown in the table given below :—

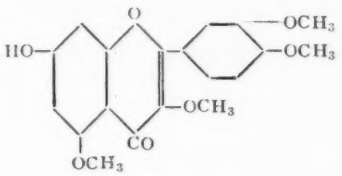
	3 : 7 : 8 : 4′-tetramethyl herbacetin	3 : 5 : 8 : 4′-tetramethyl herbacetin	The tetramethyl ether obtained by the hydrolysis of the methylated glucoside
Melting point	159–60	269–70	269–70
Solubility in sodium hydroxide ..	Difficultly soluble	Easily soluble	Easily soluble
Colour with ferric chloride solution	Bright green colour	No characteristic colour	No characteristic colour

Hence the glucose residue occupies position 7 in Herbacitrin (I, R = $C_6H_{11}O_5$) and the course of the reaction can be represented thus :—

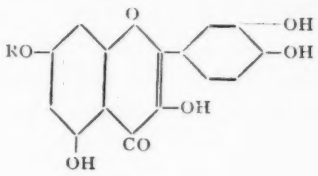


(R′ is acetylated or partially methylated glucose residue)

Quercimeritrin, a glucoside of Quercetin was originally isolated by Perkin[7] from the Egyptian cotton flowers and has since been shown to occur in *Prunus emarginata*,[8] *Helianthus annus*,[9] *G. hirsutum*,[10] *G. indicum*,[2] etc. The constitution of this glucoside was established by Attree and Perkin[11] by methylation with diazomethane and subsequent hydrolysis. We have now examined the suitability of the new method starting with the acetyl derivative of Quercimeritrin.* All the available phenolic hydroxyl groups are easily methylated and the methylated glucoside, after hydrolysis, yields 3 : 5 : 3′ : 4′-tetramethyl quercetin (VI) thus confirming the constitution of Quercimeritrin as a 7-glucoside (VII, R = $C_6H_{11}O_5$).



(VI)



(VII).

Experimental

3 : 5 : 8 : 4′-*Tetramethyl herbacetin from Herbacitrin*

Acetyl herbacitrin was prepared in the usual way by boiling Herbacitrin with acetic anhydride and anhydrous sodium acetate for 4 hours. It crystallised readily from alcohol as long needles melting at 222–24° and not at 214–16° as stated previously.[3]

Herbacitrin acetate (150 mg.) was dissolved in acetone (10 c.c.) and treated with dimethyl sulphate (1·5 c.c.) and 20% sodium hydroxide (1·5 c.c.). After shaking vigorously for sometime, more of methyl sulphate (2 c.c.) and 20% alkali (2 c.c.) were added alternately in small amounts shaking vigorously after each addition. Finally 2 c.c. more of the aklali were added to keep the medium strongly alkaline. As usual heat was gradually developed during the course of the reaction. After leaving overnight, the contents were refluxed on a water-bath for an hour. On driving off the solvent (acetone) almost completely the methylated glucoside separated out as a brown semi-solid mass. As the quantity was small, no attempt was made to isolate and purify it. In order to hydrolyse it, alcohol (25 c.c.) and water (25 c.c.) were added along with sufficient quantity of concentrated sulphuric

* This was felt to be particularly necessary since diazomethane fails to effect complete methylation in many cases.

acid so as to render the solution 7% acid and then boiled under reflux for 2 hours. The substance soon went into solution. After the hydrolysis was over, almost all the alcohol was distilled off, when a pale yellow solid separated out on cooling. It was filtered and crystallised from alcohol twice (using a little animal charcoal). It was thereby obtained in the form of golden yellow rectangular plates melting at 269–70°. (Found in air-dried specimen : OCH_3, 32·7% ; $C_{15}H_6O_3(OCH_3)_4$, H_2O requires : OCH_3, 33·0%.) It corresponded to 3 : 5 : 8 : 4′-tetramethyl herbacetin in all its properties. In alcoholic solution it imparted no colour to ferric chloride and dissolved easily in dilute sodium hydroxide and concentrated hydrochloric acid to produce yellow solutions.

On further methylation with dimethylsulphate and aqueous alkali it yielded the pentamethyl herbacetin melting at 156–58°. Mixed melting point with an authentic sample was undepressed.

3 : 5 : 3′ : 4′-*Tetramethylquercetin from Quercimeritrin*

Quercimeritrin acetate (300 mg.) was dissolved in acetone (20 c.c.) and methylated as described in the case of Herbacitrin acetate, using the proportionate amounts of dimethyl sulphate and 20% alkali. After the removal of the solvent on the water-bath, the methylated glucoside came down as a pale yellow substance. It was then hydrolysed with 100 c.c. of 7% sulphuric acid. On cooling the contents, a pale yellow substance was obtained, which was rendered pure by crystallising twice from acetic acid. It came down in the form of pale yellow needles and melted at 284–85° corresponding to 3 : 5 : 3′ : 4′-tetramethylquercetin. (Found : OCH_3 30·5 ; $C_{15}H_6O_3(OCH_3)_4$, $3H_2O$ requires : OCH_3, 30·1%.) Like the above tetramethyl ether of quercetin the substance easily dissolved in dilute sodium hydroxide to give a yellow solution and gave no characteristic colour with ferric chloride. Further treatment of this substance with dimethyl sulphate and alkali produced pentamethyl quercetin melting at 151–53°.

Summary

The constitution of Herbacitrin is established as the 7-glucoside of Herbacetin by methylating the glucoside through the acetyl derivative and isolating 7-hydroxy-3 : 5 : 8 : 4′tetramethoxy flavone from the hydrolysis of the methylated glucoside. Similarly, the constitution of Quercimeritrin is confirmed as the 7-glucoside of Quercetin.

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